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PHYSICAL CHEMISTRY FOR COLLEGES

A COURSE OF INSTRUCTION BASED UPON THE FUNDAMENTAL LAWS OF CHEMISTRY

BY

E. B. MILLARD

ASSISTANT PROFESSOR OF PHYSICAL CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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PREFACE

This book has been prepared to bring before college students certain of the more important aspects of physical chemistry, together with accurate modern data which illustrate the applicability of its laws to the phenomena observed in the laboratory. It has been assumed that the student is familiar with inorganic and analytical chemistry, that he has had an adequate course in college physics, and that the simple processes of calculus are familiar to him.

No attempt has been made to cover the whole of physical chemistry in a single volume; its most important topics have been treated at such length as the size of the volume allows, and numerous references to recent periodical literature are included for those who would pursue any given topic further.

The limitations of the orthodox laws of physical chemistry have been emphasized more than is commonly done in beginning courses of physical chemistry. To this end the illustrative data have been carefully chosen from modern experimental work, in order to minimize the "experimental errors" which are so often used to conceal real deviations of a law from the facts it is intended to express. A trusting belief in inadequate physical laws will only retard the scientific progress of a student, and weaken his faith in adequate laws; whereas a wholesome appreciation that physical chemistry is an unfinished and growing science may stimulate thoughtfulness and research. The proper time to encourage a research attitude is in the very beginning of a student's chemical career.

A qualitative treatment of the subject, so-called descriptive physical chemistry, may be obtained from the text alone; but careful consideration and study of the numerous tables of data will be required if anything approaching an appreciation of quantitative physical chemistry is desired. A quantitative point of view has been maintained as far as possible, even in the descriptive material.

Rather more tabulated data has been presented than might seem necessary in a beginning text. This is done to furnish the

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basis for numerous problems of a quantitative character. Many such problems should be solved in the course of a term, since they stimulate interest and increase the usefulness of the material taught in the class room. The problems at the end of each chapter will not be sufficient to test the ability of general classes; they are type problems in many instances, and should be supplemented by others designed by the teacher to suit the needs and ability of his particular class. Problems should often be assigned for which data must be obtained directly from tables in the text. Much of the value of problem working is lost when a student knows he must use all of the data given him and no other; this too often results in suggesting the entire solution of the problem. Moreover, fresh problems must be given every year if fresh interest in physical chemistry is maintained; this can be done only when ample data are at hand. Some of the more difficult problems at the end of a chapter should be worked by the instructor in class.

References to original sources are not intended primarily as citations of authority for statements made; they are first of all suggestions for further reading. With this in mind, most of the references are to periodicals in English, and to those which are available in small libraries. The author has not hesitated to draw upon little known periodicals when the material to be obtained in them suited the needs of the text; he has not ignored foreign publications in the search for material; but for obvious reasons much of the best data is published in the widely circulated journals, and to these most of the reference work is confined.

The author is greatly indebted to Professor James F. Norris and to Mr. Charles R. Park for reading the manuscript and making many helpful suggestions and criticisms based on their teaching experience. Their assistance has aided materially in detecting errors. He is also indebted to many other friends for kindly interest and encouragement during the preparation of the manuscript. It will be considered a favor if those who find errors of any kind in the text will communicate them to the author.

E. B. MILLARD.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASS., *March*, 1921.

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PHYSICAL CHEMISTRY FOR COLLEGES

CHAPTER I

INTRODUCTION. DETERMINATION OF ATOMIC WEIGHTS

Physical Chemistry treats of the applications of fundamental physical laws and theories to the phenomena of chemistry. A proper understanding of these laws and their applications enables us to predict, for example, the conditions under which certain chemical substances are at equilibrium, or the extent and velocity of reactions which takes place between them. The usefulness of these calculations will be apparent from the many applications cited in the following pages.

Laws of Nature.—Some of the general laws relating to chemistry are absolutely exact; they describe faithfully the most carefully conducted experiments; apparent deviations of these laws become less and less as the manipulative skill employed in testing them increases. Among these may be mentioned the indestructibility of matter (conservation of matter), the law of definite proportions, and Faraday's law of electrolysis. Other laws exhibit deviations which are not due to experimental errors, and which are of considerable magnitude. They are approximations which show in a qualitative way the behavior of substances, and which more or less accurately describe their quantitative relations. Thus no law is known which expresses exactly the change of pressure of a gas as the volume is decreased; but laws are known which show this change to within less than 1 per cent for moderate variations in volume.

We shall compare each law with the results of experiment, and aim to form an opinion as to whether judgment is required in the use of a "law," or whether it is rigidly accurate under all conditions. Some approximate laws describe the results of experiment quite accurately under certain conditions, but deviate to a larger extent under other conditions. When this is the case, the limiting conditions under which the law is accurate to within 1 or 2 per cent will be stated.

The statements put forward as laws of nature are sometimes the result of experience alone (empirical laws). There is in these cases a possibility that some future experience will demonstrate the untruth of what we have considered as a law, but the probability of this becomes less and less as the number of experiments increases. No change has ever been observed in the total mass of the substances involved in a chemical reaction; that is, no matter has ever been destroyed in changing it into other forms. As the methods of experiment have become more and more refined, and as the experimenters have become more skilful in their work, this law remains unshaken as a statement of universal experience, and it is now commonly accepted as an exact law of nature. But it has never been demonstrated that such a change of mass, or a destruction of matter, is absolutely impossible. Other simple laws, such as Boyle's law for gases, are also the result of experience, but as the experimental methods have become more refined, real deviations of these laws from the facts observed have been discovered. These experiences point to a failure of the known laws to explain completely the behavior of substances, and are not to be traced to errors of experiment.

There is another type of law which is not the result of experience, but which may be derived from a proper combination of the consequences of other laws based on experience. Thus, a great many equations expressing laws of nature may be derived from the exact law of the conservation of energy (also called the first law of heat or of thermodynamics) and from the law limiting the conversion of heat into work (the second law of thermodynamics). They are called thermodynamic laws. Since the fundamental laws are rigidly exact, the deductions based on them are also exact. But the equations so derived are often combined with less exact laws (for example, the ideal gas law). These combined expressions are therefore no longer based on thermodynamics alone, and they may fail to express accurately the known facts to which they relate. Examples of the various kinds of laws will be encountered frequently in the following chapters.

Proper reserve should always be exercised in drawing general conclusions from a set of experimental data. The phenomena of nature are often more complex than we think, and what appears to be a general law is often true only under restricted conditions. A statement of such a law without at the same time mentioning the conditions under which it is true is therefore a misrepresentation of the facts.

Theories are plausible beliefs advanced to explain observed facts. They serve to guide further experiments in a given field, but are often incapable of direct proof. Thus the theory that a gas consists of molecules, separated from one another by considerable distances and in rapid motion, offers a ready explanation of the compressibility of gases, of their diffusion, of their ability to mix with other gases in all proportions, and of practically all their properties, but the theory is not capable of direct proof. That is, no one has been able to see or experiment with a single gaseous molecule. The evidence in favor of the truth of the theory is, however, abundant and convincing; no facts are known which contradict it; and deductions based on this theory are in accord with the results of experiment. It is therefore universally accepted as a fact, but is referred to as the kinetic *theory* of gases.

Many such theories are found in chemistry. They are accepted so long as they are in accord with the facts; they may be altered to fit new discoveries, but they should be discarded in favor of newer and more satisfactory ones when they seriously conflict with the results of experiments.

Indestructibility of Matter.—It is a familiar fact that matter can be changed into various forms (by combination and rearrangement of the elements in various ways) without any loss in the total mass of material. In other words the total mass of all the substances taking part in a chemical reaction is unchanged by the reaction. The many operations of analytical chemistry depend on the validity of this fact; but since there is no reason why there *might* not be a change of mass during chemical change, it has been necessary to test this belief experimentally before accepting it as a fact. Perhaps the best known tests of this character are Landolt's experiments[1] extending over a period of 20 years, and devoted to a careful study of 15 different chemical reactions, which were examined with great skill and care. The reacting substances were enclosed in the separate arms of sealed vessels, such as that of Fig. 1, to prevent the possibility of mechanical loss of material. The tubes were weighed on a very sensitive balance, using a counterpoise of the same size and shape. Then by tipping the vessel, the two solutions were brought in contact a little at a time, so that any heat effect of the reaction would not expand the bulb and thus cause an apparent change in weight by increasing its air displacement. After the reaction had been completed the vessel was weighed again. The weighings were made several times, and an average taken. As a result of his work, Landolt concluded that if there was a change in mass during chemical reaction, it was less than the error of weighing, which was about one part in 10,000,000.

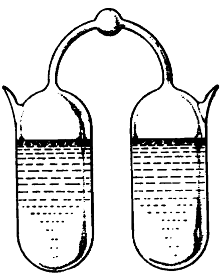

FIG. 1.

The later work of Manley[2] on the reaction $6AgNO_3 + 6FeSO_4 = 6Ag + 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6$ was carried out with exceeding care. Two tubes of the form shown in the figure were filled with silver nitrate solution in one limb and ferrous sulfate solution in the other, and their weights were made as nearly equal as possible, after which the tubes were sealed shut and hung on the arms of a very sensitive balance. After a series of careful weighings extending over a period of several days, it was determined that the difference in weight of the two tubes was 0.026 mg. in one experiment. The contents of one tube were mixed, causing the reaction given above to take place, and after a time the difference in weight was again determined. Now if there is a change in mass during chemical reaction, the difference in weight between the two tubes should change, as a reaction has taken place in one of them and not in the other. After the reaction the difference in weight between the two tubes was found to be 0.022 mg., which corresponds to a change of 0.004 mg. Since the total weight of reacting substance was about 127 grams, the change in weight was one part in 32,000,000, which is again less than the probable error of the weighing. In another series of experiments the reaction between barium chloride and sodium sulfate was examined with the same care, and it was shown that any change in weight must be less than one part in 100,000,000.

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[1] *Z. physik. Chem.*, **12,** 1 (1893); *Sitzb. Preuss. Akad. Wiss.*, **1908,** 354.

[2] *Phil. Trans. Roy. Soc. London* (*A*) **212,** 227 (1913).

In making these weighings the balance was carefully maintained at a constant temperature and shielded from air currents; the tubes were handled by a system of levers so as to protect the balance from heat from the body of the operator; and a period of some days elapsed between the chemical reaction and the final set of weighings. During this time the tube was kept under a bell jar and otherwise protected from dust or contamination of any kind.

In the light of these experiments there is no room for doubt as to the exactness of the law of indestructibility of matter. We may therefore state as an *exact* law of nature that matter (anything which has mass) does not change in mass during combination or chemical decomposition.

Elements and Compounds.—The number of kinds of matter is very great indeed, but attempts to resolve matter into its ultimate constituents have brought to light about 92 substances which cannot be decomposed into simpler substances. These are called elements. The number of experiments performed upon the known elements is so great as to make it improbable that any of them consist of two substances which may be separated later by some chemical process. There are a few more elements yet to be discovered, but the periodic arrangement of the elements makes it probable that the number of undiscovered elements is small. Thus, the discovery of an element similar to manganese and of higher atomic weight would not disturb the periodic arrangement, for in the periodic table it was necessary to leave a blank corresponding to such an element. But the discovery of an alkali element with an atomic weight between sodium and potassium would give us an element for which there was no place in the periodic table, and thus disturb this arrangement. Hence, the existence of such an element is improbable. All of the known kinds of matter consist of combinations of these elements in various proportions. Practically all kinds of matter have been decomposed into their elements, or into simple compounds which may be so decomposed, and a vast number of the substances in nature have been built up from the elementary substances in the laboratory. In addition, many substances not found in nature have been so made. Certain substances, notably the complex compounds occurring in plants and animals, have not so far been prepared synthetically.

Law of Definite Proportions.—This law states that the quantity of an element which will combine with a given weight of another element to form a pure chemical compound is a fixed quantity, regardless of the method of preparation of the compound. In other words, the percentage of each element in a pure compound is always the same, and the presence of an excess of one element does not result in the formation of a compound containing more of it.

Table 1 shows data[1] on the synthesis of silver bromide from carefully purified silver and bromine, together with the weight of bromine combined with each gram of silver. Elaborate precautions were taken to assure the purity of the substances weighed, and to avoid mechanical loss during the synthesis.

TABLE 1

Weight of silver	Weight of silver bromide formed	Grams of bromine combined with each gram of silver
5.01725	8.73393	0.74078
5.96818	10.38932	0.74079
5.62992	9.80039	0.74077
8.13612	14.16334	0.74080
5.07238	8.82997	0.74079
4.80711	8.36827	0.74081
5.86115	10.20299	0.74078
6.38180	11.10930	0.74078
6.23696	10.85722	0.74079
9.18778	15.99392	0.74078
8.01261	13.94826	0.74079
8.59260	14.95797	0.74079
8.97307	15.62022	0.74079
		Average 0.74078

---

[1] Baxter, *J. Amer. Chem. Soc.*, **28**, 1322 (1906).

The synthesis was conducted by supplying ammonium bromide to a weighed quantity of silver which had been converted into nitrate, until no more bromine would combine with the silver, after which the silver bromide was collected and weighed.

Another example of the law of definite proportions is shown in Table 2. A quantity of iron was converted into ferric oxide and heated with an excess of oxygen until no more would combine with it.[1] The ferric oxide was weighed, then heated in a current of hydrogen until all of the oxide had been completely reduced to iron, which was then weighed.

TABLE 2

Weight of iron	Weight Fe_2O_3	Per cent Fe in Fe_2O_3
2.78115	3.97557	69.956
3.42558	4.89655	69.959
3.04990	4.35955	69.959
4.99533	7.14115	69.951
4.49130	6.42021	69.956

The synthesis of tin tetrabromide is shown in Table 3. It will be seen again that the composition of the product is constant,[2] in so far as it is possible for the best quantitative chemistry to determine it.

TABLE 3

Weight of tin	Weight of $SnBr_4$ formed	Per cent tin in $SnBr_4$
2.8445	10.4914	27.113
4.5735	16.8620	27.123
4.5236	16.6752	27.119
3.0125	11.1086	27.116
2.8840	10.6356	27.113
3.0060	11.0871	27.123

Molecular Theory.—The theory that matter of all kinds consists of very small particles or molecules, is now commonly accepted as a fact. This theory is in complete accord with all the known facts of chemistry; it explains in a simple way all of our chemical reactions; and it forms the basis of modern chemical thinking. The molecules of which a substance consists cannot be divided into smaller particles without a complete change in the properties of the resulting particles. They are the limit of divisibility for a given kind of matter. When all of the molecules in a mass of matter are exactly alike, this mass of matter is called a *pure substance*. When there are two or more kinds of molecules present the mass of matter is called a *mixture*. A pure substance may be prepared from one containing other kinds of substances by treating it with a solvent which will dissolve one substance and not the others, by distilling it if the undesirable substances are not volatile, by treating it with a reagent which will convert the undesirable matter into an insoluble form or a volatile form, by crystallizing it several times from some solvent, etc. It is probably true that we are unable to prepare specimens of a substance which contain only one kind of molecule, but when the other molecules have been so far eliminated that their effect is not detectable by our most sensitive means, we call the resulting product a pure substance.

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[1] Richards and Baxter, *Proc. Am. Acad. Sci.*, **35**, 253 (1900).

[2] Bongart and Classen, *Berichte*, **21**, 2900 (1888).

If all of the molecules of a pure substance are exactly alike, each of them must contain the same percentage of each constituent element as the whole mass of substance. It is certain that all of the molecules must be exactly alike in every respect, for otherwise by availing ourselves of the properties in which they differ we could effect a separation into two portions having different properties, that is, into two pure substances. Hence every molecule must have the same composition as the whole mass of pure substance. Two matters at once claim interest; the relative weights of the molecules of different substances, and the way in which the molecules are formed from their constituent elements.

The relative molecular weights cannot be determined from comparisons of single molecules, on account of their small size. But equally satisfactory results may be obtained if we had a way of counting out the same number of molecules of each substance for comparison. Avogadro's law furnishes such a method.

Avogadro's Law.—This law states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. As this law is discussed in some detail in the next chapter we will not take up here the line of thought on which it is based or the proof of its validity. In order to determine the relative weights of the molecules of two substances, we need only compare the weights of equal volumes of them in the gaseous state under similar conditions, since we are then comparing equal numbers of molecules. Naturally the next step is to adopt some substance as a standard of reference for relative molecular weights, and chemists now by common consent have adopted 32 as the "molecular weight" of oxygen. Since they employ the gram as a unit of weight, 32 grams of oxygen is therefore accepted as a "gram-molecular weight," or a gram-molecule. On account of the extensive use of this term, it has been abbreviated to "mol," which is written without a period. It is not an abbreviation of the word molecule, but a separate new word meaning "gram-molecular weight."

A **molecular weight** of a gas is that weight of it which occupies, under any conditions of temperature and pressure, the same volume as a molecular weight (32 grams) of oxygen under these same conditions. "Standard" conditions are a temperature of 0° and a pressure of one atmosphere, but it should be made clear that comparisons are not restricted to these experimental conditions. A **molecular volume** of a gas is the volume of 32 grams of oxygen. Then *the molecular weight of a gaseous substance is that weight of it which occupies a molecular volume.* We may of course determine the molecular volume under any convenient conditions from the volume of 32 grams of oxygen, and compute the weight of a molecular volume from the weight of any known volume. Experimental procedures for this are described in the next chapter.

The choice of 32 as the molecular weight of oxygen is in conformity with 16 as its atomic weight. The following reasoning will show that the two numbers are not separate standards.

One volume of oxygen and two volumes of hydrogen combine to give two volumes of water vapor. Avogadro's law therefore requires that the number of molecules of water vapor formed be equal to the number of hydrogen molecules used, and that it be twice the number of oxygen molecules used. But each molecule of water must contain a whole atom of oxygen, since the atoms are indivisible, and it follows that the oxygen molecules contain two atoms each. In conformity with our choice of 32 for the molecular weight of oxygen, which often forms compounds containing only a single atom per molecule, it will be necessary to take 16 as its atomic weight. Thus 32 grams of oxygen will contain the same number of molecules as 16 grams of oxygen contains atoms

Atomic Weights.—Mention has been made of the fact that molecules of compound substances contain more than one kind of element. A molecule is therefore not the smallest division of matter, though it is the smallest one capable of separate existence. The parts of molecules are called atoms, and molecules are made of a whole number of atoms, since these are defined as the smallest particles of matter. When a pure substance is an elementary one, all of the atoms in its molecules are exactly alike. The number of atoms in a molecule of an element may be one (as in helium and argon, the vapors of metals, and other substances at very high temperatures), two (in most of the common elementary gases) or more, but the atoms are all exactly alike, since when these elements react with another elementary substance, there is only one kind of product formed. When the molecule (the particle capable of separate existence) contains only a single atom, the atomic weight is identical with the molecular weight. If an elementary molecule contains two atoms its atomic weight is half of its molecular weight. Thus the molecular weight of hydrogen is two, and its atomic weight is one; just as the choice of 32 as the molecular weight of oxygen made necessary 16 as its atomic weight.

An atomic weight of an element is the smallest weight of it found in a gram-molecule of any of its compounds. A molecule must contain a whole number of atoms of any element; a gram-molecular weight of a compound contains a whole number of atomic weights of each element in it. Thus the accepted values of atomic weights represent the smallest quantity of each element found in a gram-molecule of any compound so far; and the possibility of discovering a compound with less of the element per molecular weight always exists. The probability of this discovery becomes less as the number of compounds studied increases. There are also other ways in which the value of an atomic weight may be checked, such as its specific heat, its place in the periodic system, and the relation between its compounds and other similar compounds. The atomic weights given in the table on page 16 are probably the true ones in every case.

Atomic Weight Methods.—(*a*) *From Gas Densities Alone.*—In cases where the number of atoms in a molecule of an elementary substance has been established from the volumes of the gaseous substances formed by it upon reaction with other gases, the atomic weight may be determined by dividing the molecular weight by the proper whole number. Similarly the atomic weight of bromine may be determined by subtracting from the molecular weight of hydrogen bromide the atomic weight of hydrogen, since its molecule is known from combining volumes to contain one atom of each element. But Avogadro's law is one which becomes more exact as the gases under comparison are studied at lower pressures. On the other hand, the difficulty of determining the weight of a volume of gas increases as the pressure is reduced, since the quantity of substance weighed becomes smaller in comparison to the weight of the vessel in which it is contained. Skillful work will overcome the last mentioned difficulty, but from the deviations of Avogadro's law at higher pressures there is no escape. The problem of determining exact gas densities at pressures for which Avogadro's law is also exact has been solved by the careful experiments of Guye and his students. Their work on methyl fluoride[1] may serve as an illustration of the method, and of the results obtained. The weight of a liter of gas at 0° was determined for pressures of one atmosphere, two-thirds of an atmosphere, and one-third of an atmosphere; and from these figures a value of d/p at 0° was calculated for each pressure. These values represent the weight which a liter of methyl fluoride would have at one atmosphere if the deviation of Avogadro's law were as small as they are at the pressure of the determination. The data are shown in Table 4.

The deviations become smaller at still lower pressures, but the quantity of gas to be weighed is too small for accurate work. They therefore plotted the values of d/p against the pressure and (since the points come on a straight line) extended the line to where it cuts the axis of zero pressure. This gives the "limiting

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[1] Moles and Batuecas, *J. chimie physique*, **17**, 537 (1919).

TABLE 4

Pressure (atmospheres)	Weight of a liter of methyl fluoride at 0° (grams.)	Ratio d/p
1.0000	1.5454	1.5454
0.6667	1.0241	1.5361
0.3333	0.5091	1.5269

density" or the weight of a liter of the substance if it behaved as an ideal gas. As will be seen from Fig. 2, this value is 1.5177.

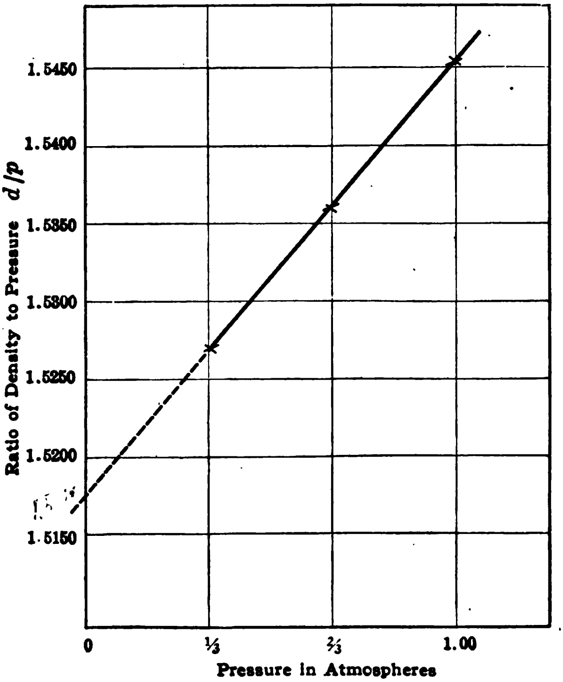

FIG. 2.

Since the volume of a mol of ideal gas under standard conditions is 22,410 c.c., the exact molecular weight of methyl fluoride is 22.410×1.5177, or 34.012. The formula is CH_3F, and the atomic weights of carbon and hydrogen are accurately known, namely

12.00 and 1.008 respectively. Thus 12.00 + 3 × 1.008 + F = 34.012, from which the atomic weight of fluorine is 18.99.

(*b*) *From Molecular Weights and Compositions by Weight.*—A molecular weight of a compound must contain a whole number of atomic weights of each element in it. When large numbers of gaseous compounds of any element are examined, the smallest weight of an element found in a mol of any of its compounds is called the atomic weight of that element. On account of the fact that determinations of molecular weight are not usually performed with great accuracy, careful analytical work is used to supplement this work. An example will make this point clearer. In the following table are given some approximate data for gaseous nitrogen compounds, using only whole numbers.

TABLE 5

Substance	Weight of a molal volume of gas	Per cent nitrogen in the compound	Weight of nitrogen in a mol of gas
Nitric oxide	30	47	14
Ammonia	17	82	14
Nitrous oxide	44	64	28
Nitric acid	63	22	14
Nitrosyl chloride	66	21	14
Hydrazine	32	87	28

It is seen from this table that no nitrogen compound contains less than 14 grams of nitrogen per molecular weight; this is then the approximate atomic weight. But it is not an *exact* value, since it is based on rough data. An accurate value may, however, be obtained from a quantitative analysis of nitric oxide or nitrosyl chloride, since exactly one atomic weight of nitrogen combines with exactly 16 grams of oxygen in each case. The following analyses[1] show the composition of nitrosyl chloride. From the average of these figures may be obtained the ratio N : O : Cl = x : 16.000 : 35.458, leading to an *exact* atomic weight of nitrogen, namely 14.006, based on a known atomic weight for chlorine.

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[1] Guye and Fluss, *J. chimie physique*, 6, 732 (1908).

TABLE 6

Weight of NOCl	Weight of chlorine	Weight of oxygen	Weight of nitrogen	Loss
0.5341	0.2893	0.1305	0.1142	0.0001
0.4284	0.2319	0.1046	0.0916	0.0003
0.7995	0.4331	0.1954	0.1710	0.0000
0.5121	0.2773	0.1251	0.1095	0.0002

(*c*) *From Analytical Data and Specific Heats.*—The metals and some other elements do not form gaseous compounds at temperatures suited to accurate work, and determinations of their atomic weights must therefore rest on other considerations. But the weight of a metal which combines with 16 grams of oxygen is either an atomic weight, two atomic weights, half an atomic weight, or two-thirds or three-fourths or two-fifths of an atomic weight, depending on whether the formula of the oxide is EO, E_2O, EO_2, E_2O_3, E_3O_4 or E_2O_5. Analysis of the oxide will give therefore an exact value of the atomic weight, or a simple fraction of it, and it requires only a rough determination in some other way to indicate which multiple of the weight combined with 16 grams of oxygen is the true atomic weight. The **law of Dulong and Petit** furnishes such a method of fixing the multiple for metals and the heavy elements. This law states that the atomic heat capacity of solid elements is about 6.2, that is, that the quantity of heat required to raise an atomic weight of an element through a degree is the same for all solid elements. The heat capacity of a gram multiplied by the atomic weight is therefore 6.2, or the atomic weight is 6.2 divided by the heat capacity of a gram of element. From the data of Table 2 we see that iron oxide is 69.956 per cent iron; hence the weight of iron combined with 16 grams of oxygen is $x : 16 = 69.956 : (100.00 - 69.956)$, or $x = 37.256$. This is either the atomic weight of iron or a simple fraction of it. The specific heat of iron is 0.115, and 6.2 divided by 0.115, is 54, which is approximately the true atomic weight. It will be seen that 37.256 is about two-thirds of 54, whence the true atomic weight is 1.5×37.256 or 55.88.

The atomic weight of bromine has been established by methods (*a*) and (*b*) at 79.92. From this we may compute the atomic weight of silver from the data of Table 1, since an atomic weight of silver combines with a whole number of atomic weights of bromine. Thus $Ag : Br = 1.000 : 0.74078 = x : 79.92$, whence $x = 107.88$. The specific heat of silver is 0.056, and 6.2/0.056 is 110. Thus the true atomic weight of silver is 107.88.

An example of a more complete set of experiments is the following one, which serves to determine the atomic weights of silver, chlorine and lithium with reference to oxygen. By reducing lithium perchlorate to chloride it was found[1] that 100 grams of the former gave 39.845 grams of the latter. The formula of the perchlorate is $LiClO_4$, whence it follows that the molecular weight of lithium chloride is $x : (x + 4 \times 16.00) = 39.845 : 100.000$, or $x = 42.393$. The lithium chloride was then treated with silver nitrate solution made from a weighed quantity of silver, from which it was found that each gram of lithium chloride required 2.54460 grams of silver, giving the atomic weight of silver as 2.54460 times the molecular weight of lithium chloride, or 107.871. This will be seen to be in accord with its atomic weight calculated above from the synthesis of silver bromide. Then by weighing the silver chloride formed the ratio of silver to silver chloride was found to be 1 : 1.3287, from which the atomic weight of chlorine is given by $107.871 : (107.871 + y) = 1.000 : 1.3287$, or $y = 35.454$. Returning now to the ratio of lithium chloride to perchlorate, we see that the atomic weight of lithium may be calculated from the atomic weight of chlorine just found. $LiClO_4 : LiCl = z + 35.454 + 4 \times 16.000 : z + 35.454$, or as $100.000 : 39.845$, whence $z = 6.939$.

The atomic weight table published each year is based on all of the determinations made by various methods, the weight assigned to each determination in computing the value for a given element being determined by the number of experiments in a series and the probable error of the average value. These calculations are made by an International Commission appointed for the purpose by the largest chemical societies of the world The atomic weight of an element is changed when new experiments show that the accepted value is in error, in the opinion of the members of the International Commission. All of the figures stated are

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[1] Richards and Willard, *J. Am. Chem. Soc.* **32**, 4 (1914).

TABLE 7.—INTERNATIONAL ATOMIC WEIGHTS,[1] 1921

	Symbol	Atomic weight
Aluminum	Al	27.1
Antimony	Sb	120.2
Argon	A	39.9
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	10.9
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.1
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	70.1
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.008
Osmium	Os	190.9
Oxygen	**O**	**16.00**
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	45.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.15
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	89.33
Zinc	Zn	65.37
Zirconium	Zr	90.6

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[1] *J. Amer. Chem. Soc.*, **42**, 1763 (1920).

significant. Thus 14.008 for nitrogen indicates that this atomic weight is accurate to a thousandth of a unit, 27.1 for aluminum indicates that the second decimal place is still uncertain. Table 7 gives the atomic weights for use in 1921.

A summary of all the atomic weight work done prior to 1910 is given in the Smithsonian miscellaneous collections, volume 54, number 3. Work done since that time is summarized each year in connection with the report of the International Committee on atomic weights.

Units and Standards.—It will be convenient here to define and record the numerical values of some of the terms used throughout the book. We shall use the centimeter-gram-second system of units and the Centigrade temperature scale, most of the units of which are familiar from work in physics and chemistry.

A **liter** is the volume of 1,000 grams of water at a temperature of 4°C.

A **kilo** is a thousand grams, and is the abbreviation of kilogram commonly employed.

A **mol** is the molecular weight of a substance in grams. This term is identical with gram-molecule or gram-molecular weight.

A **calorie** is the quantity of heat required to raise a gram of water from 15° to 16°. It is abbreviated cal.; and the large calorie which is a thousand small calories is written Cal. A small calorie is 4.182 **joules,** or 4.182×10^7 **ergs.**

A **dyne** is the force which will impart to a gram mass a velocity of one centimeter per second in a second. The acceleration of **gravity** at sea level and 45° latitude is 980.6. An **erg** is the work done by a force of one dyne acting through a distance of one centimeter.

Pressure is the force acting on a unit area. The absolute unit is one dyne per square centimeter, or one **bar.** A million bars is one **megabar,** which is very nearly the pressure of the atmosphere at sea level. Pressures are also commonly stated in atmospheres; a pressure of one **atmosphere** will support a column of mercury at 0° C, 76.00 cm. high at a point where the acceleration of gravity is normal, that is, at 45° latitude and at sea level. The force of one atmosphere is therefore $76.00 \times 13.60 \times 980.6 = 1{,}013{,}200$ bars, or 1.0132 megabars (13.60 being the mass of a centimeter cube of mercury at 0°): In spite of the convenient size of the megabar unit, which is more nearly the average atmospheric pressure than the standard atmosphere, the latter remains the common unit of pressure in scientific work. The adoption of the absolute unit has been strongly urged, but largely on account of the definition of boiling points and of the Centigrade temperature scale in terms of the standard atmosphere, the megabar has not come into common use.

The work done when a piston of one square centimeter area moves one centimeter against a pressure of one atmosphere is called a **cubic-centimeter-atmosphere.** This quantity of work is done for each cubic centimeter increase in volume during evaporation of a liquid at atmospheric pressure, that is, at the boiling point of the liquid. One small calorie is equivalent to 41.24 c.c.-atmospheres, or one c.c.-atmosphere is equivalent to 0.02425 cal.

Temperature is measured on the Centigrade scale, on which the melting point of ice under a pressure of 1 atmosphere is 0° and the boiling point of water under a pressure of 1 atmosphere is taken as 100°. The **absolute scale** (or Kelvin scale) consists of Centigrade degrees, but takes its zero point 273.09°[1] lower than the melting point of ice, for reasons explained in the next chapter. On this scale water therefore boils at 373.09.

In chemical considerations the formula weight is a more convenient unit of quantity than the gram, and it is more definite than the chemical equivalent, which may be different for a substance taking part in different reactions. A formula weight of substance is that weight of it in grams which is the sum of the atomic weights of the elements in its chemical formula. Thus, 63.57 + 32.06 + 64 or 159.63 grams of $CuSO_4$ is a formula weight of the anhydrous substance, but 159.63 + 5 × 18.016 or 249.71 grams of the blue crystals make a formula weight of $CuSO_4.5H_2O$.

Concentration.—When a formula weight of a substance is dissolved in a liter of solvent, a formal solution results. This will not in general be exactly a liter of solution, but a formal solution is defined in this way to facilitate calculating mol

[1] Keyes gives 273.14°, *J. Am. Chem. Soc.*, **42**, 54 (1920).

fraction (to be defined later) from concentration. We shall define a normal solution as in volumetric analysis: one containing a chemical equivalent of substance in a liter of solution. When the properties under consideration depend on the relative quantities of solvent and dissolved substance, formal concentrations will be employed. These are in general identical with molal concentrations, since the formula is written to correspond to the molecular weight. When the properties depend on the volume of the solution, normal or equivalent concentrations will be used. In very dilute solutions a liter of solvent is contained in what is essentially a liter of solution, but the difference in volume between a solution and the solvent in it is often considerable for strong solutions.

The chief advantage in using formula weights rather than mols of solute is in connection with ionized solutes, as shown in Chapter VI. Thus we shall later define the molal lowering of the freezing point for an aqueous solution as 1.86°, but a solution of sulfuric acid having this freezing point is not a molal solution in the light of its chemical reactions. However a formal solution is one containing 96 grams of sulfuric acid, and it produces a larger depression than 1.86°, owing to its ionization into other solutes; hydrogen ions and sulfate ions. For such a solute as Na_2HPO_4 a normal solution will depend upon the reaction involved, but a formula weight is a perfectly definite quantity.

A **coulomb** is an ampere-second, or that quantity of electricity which will deposit 0.00111800 grams of silver from solution in a standard coulometer. A **faraday** is 96,500 coulombs of electricity, and it will deposit one atomic weight of silver or its chemical equivalent of some other element.

An **ampere** is a current of one coulomb per second.

A **volt** is the electromotive force of a cell such that the electrical work done by it is 96,500 joules or 23,074 cal. when the quantity of electricity passing through it is one faraday.

An **ohm** is such an electrical resistance that a potential of 1 volt across it causes one ampere current to flow; it is the resistance at 0° of a column of mercury 106.3 cm. long and one square millimeter in cross section.

Questions

✓ 1. The weight of a liter of hydrogen bromide at 0° is as follows:

Pressure	Weight of a liter
1.0000	3.6441
0.6667	2.4220
0.3333	1.2074

Compute a value of d/p for each pressure, plot these values against the pressure and extrapolate the curve. From its intercept on the axis of zero pressure calculate an exact value of the molecular weight of hydrogen bromide and of the atomic weight of bromine. The ideal molal volume at 0°C. is 22,410 c.c. and the atomic weight of hydrogen is 1.008.

2. From the atomic weight of bromine obtained in the previous problem calculate an exact value of the atomic weight of tin by means of the data in Table 3.

3. Assuming the atomic weight of silver to be 107.880, compute a value for the atomic weight of bromine from Table 1. Calculate the per cent deviation of this value from the one given in the International Table of Atomic Weights.

4. Potassium chlorate contains 39.154 per cent of oxygen, and a gram of silver when converted into silver nitrate will react with 0.691145 gram of potassium chloride. (*a*) Calculate the molecular weight of potassium chloride and the atomic weight of silver from these data. (*b*) Calculate the atomic weight of chlorine from that of silver just found and the ratio of silver to silver chloride given in the text. (*c*) Calculate the atomic weight of potassium from the composition of potassium chlorate and this atomic weight of chlorine.

5. Silver bromate contains 20.35 per cent oxygen. Calculate the molecular weight of silver bromide. Calculate the atomic weight of bromine from the data of Table 1 and the atomic weight of silver obtained in the previous problem. Compare these values with the ones in Table 7.

✓ 6. Pure silicon tetrachloride was decomposed with sodium hydroxide solution, and the chloride was precipitated with silver nitrate made from weighed portions of silver. (*J. Am. Chem. Soc.* **42**, 1194 (1920).)

Weight $SiCl_4$	Weight silver	Ratio $SiCl_4$:4 Ag
10.4353	26.4952	0.39386
5.9785	15.1830	0.39376
8.7905	22.3213	0.39381
6.8352	17.3562	0.39383

Calculate from each experiment the molecular weight of silicon tetrachloride, and calculate an average value of the atomic weight of silicon, using as the atomic weights of silver and chlorine 107.880 and 35.457. Calculate the percentage error in the value for silicon in the International table.

7. The following data (Morley) relate to the composition of water.

Weight hydrogen	Weight oxygen	Weight water
3.2559	25.8531	29.1052
3.8382	30.4700	34.3151
3.8523	30.5818	34.4327
3.8211	30.3429	34.1559

Calculate exactly the atomic weight of hydrogen from each set of weighings, and compare the average value with that in the International table.

✓ 8. Lead chloride is 74.545 per cent lead, and the heat capacity of lead is 0.029 calories per gram. Calculate exactly the atomic weight of lead.

9. Cadmium bromide is 41.29 per cent metal. From this data and its specific heat, which is about 0.05, calculate its atomic weight, assuming Br = 79.92.

10. The ratio of hydrogen to bromine in hydrogen bromide is 1.000: 79.307. From this ratio and the atomic weight of hydrogen derived in question 7 calculate the atomic weight of bromine.

CHAPTER II

PROPERTIES OF SUBSTANCES IN THE GASEOUS STATE

A gas may be defined as a substance which distributes itself uniformly throughout any space in which it is placed, whatever quantity of gas is employed, and regardless of the amount of space. It should be kept in mind that a substance may or may not be a gas, according to the conditions imposed upon it. All of the substances we refer to as gases have been liquefied at low temperatures; all except helium have been solidified. Nearly all of the common liquids and solids may be changed to the gaseous condition at high temperatures, and at low pressures. The exceptions to this statement are substances which decompose on heating. Substances such as the common metals, sodium chloride and most metallic halides are readily changed to gases by heating to a high temperature; but nitrates and sulfates, complex organic compounds and salts of organic acids generally decompose before reaching their temperature of vaporization.

When a quantity of gas cannot be separated into two fractions having different properties, such as density, solubility, or color, by any physical methods, it is a pure substance. It will be remembered that a pure substance is defined as one whose molecules are all exactly alike. Mixtures of two or more kinds of molecules exhibit most of the physical properties of a gas containing only one kind of molecules, follow the laws which describe the behavior of gases, and may usually be treated as a single gas. They should always be referred to as a mixture of gases, however.

Structure of a Gas.—On account of the ability of a gas to fill any quantity of space, it is necessary that the molecules of which it consists may be separated from one another with considerable ease. The fact that a small quantity of liquid gives a very much larger volume of vapor or gas at the same pressure is evidence that the molecules of a gas are separated from one another by considerable distances compared to the diameters of the molecules themselves. Eighteen grams of liquid water, or one molal weight, occupy 18.8 c.c. in the liquid state at 100° and 1 atmosphere pressure, but these same molecules occupy about 30 liters when changed to a gas (steam) at this temperature and pressure. Thus in the gaseous phase[1] the volume available for the use of each molecule is over a thousand times what it was in the liquid state. We do not believe that the volume of the molecules themselves has changed in size to any considerable extent during evaporation, but only that the free space around them is larger. This will be taken up in more detail in connection with the kinetic theory of gases.

The molecules of a gas are not stationary, but are moving about in space with very high velocities. They collide with each other frequently and with the walls of the containing vessel, giving rise to the pressure exerted by the gas. If the volume of the gas is increased, the number of collisions on a given area is decreased, that is, a smaller number of molecules strike any area of the wall in a given time and the pressure decreases. The pressure of a gas at constant volume increases as the temperature is raised (Gay Lussac's law, page 28), which means that there are more collisions of the molecules with the walls in a unit of time, and hence that the velocity of the molecules increases at higher temperatures. The pressure exerted by a gas does not decrease with time, so we are led to the conclusion that the collisions between molecules are perfectly elastic and that no decrease in average velocity results from a collision. The "empty space" between molecules bears some resemblance to that between the spokes of a rapidly revolving wheel. The spokes do not fill all of the space in which they revolve at any one time, but the whole of this space is effectively occupied, so that nothing else can be kept in the space. In the same manner, other molecules cannot be inserted into the empty space between molecules without increasing the number of collisions, and hence the pressure of the gas.

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[1] The homogeneous parts of any system which are separated from one another by definite physical boundaries are often called its *phases*. For example, the homogeneous parts ice, liquid water, and water vapor are the phases or states of aggregation common to water. A solution is a single phase because there are no visible boundaries between the parts of it, solvent and dissolved substance. A mixture of several gases constitutes a single phase, for gases mix in all proportions, and there is no physical boundary between one gas and another. A mixture of solids forms as many phases as there are kinds of solid present, since each is divided from the others by definite boundaries. When a single solid substance is capable of existing in two different crystalline modifications, each of these is considered a separate phase. Rhombic and monoclinic sulfur, red phosphorus and yellow phosphorus, grey tin and white tin are familiar examples of pure substances forming two different solid phases.

The treatment of gases at moderate pressures and at temperatures well removed from their condensation points is comparatively simple, for all of them have properties in common, which are expressed approximately by a few simple laws.

Boyle's Law.—This law states that at any constant temperature the volume occupied by a quantity of gas is inversely proportional to the pressure exerted upon it. While *all* substances undergo a decrease in volume with increasing pressure, it is only with gases that the volume is inversely proportional to the pressure or, as is commonly said, the "pressure-volume product" is constant at a given temperature. Very careful experiments made since the discovery of the law have shown that it is not very exact, but that it is a limiting law which describes the behavior of actual gases more closely as the pressure is decreased or as the temperature is raised. For gases under small pressures the deviations of Boyle's law are small, as shown by the following tables, and illustrated in Fig. 3.

TABLE 8.—HELIUM[1] AT 0°

Pressure in atmospheres	Volume of a molecular weight	Product
1.1021	20.65	22.41
1.0458	21.42	22.41
1.0020	22.37	22.41
0.9634	23.27	22.41
0.8067	27.78	22.41
0.7387	30.33	22.41
0.6847	32.73	22.41
0.6086	36.80	22.41
0.5387	41.61	22.41
0.4720	47.48	22.41
0.3550	63.10	22.41
0.2626	85.30	22.41
0.1937	115.65	22.41

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[1] Burt, *Trans. Faraday Soc.*, **6**, 19 (1910).

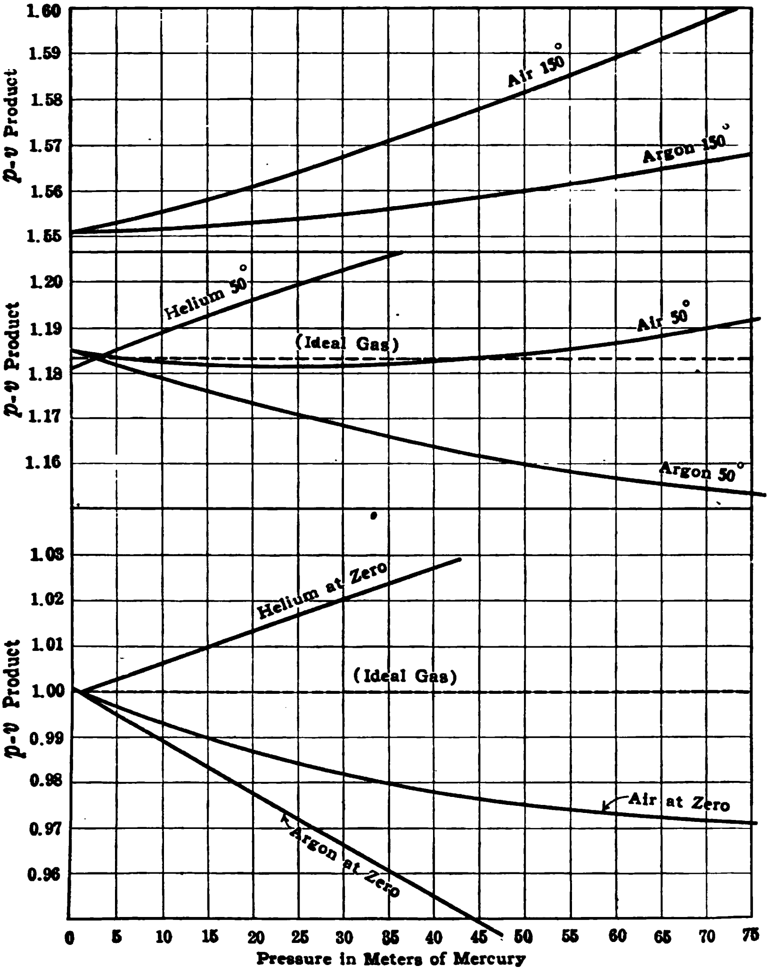
p-v Product
1.60
1.59
1.58
1.57
1.56
1.55
Air 150°
Argon 150°
p-v Product
1.20
1.19
1.18
1.17
1.16
Helium 50°
(Ideal Gas)
Air 50°
Argon 50°
p-v Product
1.03
1.02
1.01
1.00
0.99
0.98
0.97
0.96
Helium at Zero
(Ideal Gas)
Air at Zero
Argon at Zero
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
Pressure in Meters of Mercury

FIG. 3.

Table 9*a*.—Argon at Various Temperatures[1]

Pressure, meters (of Hg.)	Pressure-volume product at				
	0°	50°	100°	150°	200°
0.76	1.0003	1.1841	1.3676	1.5511	1.7346
1	1.0000	1.1839	1.3676	1.5512	1.7347
5	0.9952	1.1815	1.3666	1.5516	1.7357
10	0.9893	1.1786	1.3656	1.5522	1.7371
15	0.9833	1.1757	1.3647	1.5528	1.7387
20	0.9774	1.1730	1.3639	1.5535	1.7404
25	0.9717	1.1704	1.3633	1.5543	1.7423
30	0.9662	1.1680	1.3628	1.5552	1.7442
35	0.9609	1.1657	1.3624	1.5561	1.7463
40	0.9558	1.1636	1.3622	1.5573	1.7484
45	0.9511	1.1617	1.3620	1.5586	1.7506
50	0.9465	1.1599	1.3621	1.5601	1.7529
55	0.9422	1.1582	1.3622	1.5616	1.7553
60	0.9381	1.1568	1.3626	1.5632	1.7578
65	0.9342	1.1555	1.3631	1.5648	1.7604
70	0.9305	1.1544	1.3638	1.5664	1.7630
75	0.9270	1.1535	1.3646	1.5681	1.7658

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[1] Holborn and Schultz, *Ann. Physik*, **47**, 1089 (1915). These figures are expressed in meters of mercury as the unit of pressure, and the volume of a liter of gas under 1 meter pressure is taken as the unit quantity of gas. To obtain the molal volume in liters at any pressure given, multiply the pressure-volume value by $17.035/p$, using the value of p in meters of mercury. To convert a pressure in meters to standard atmospheres, multiply by 1.316.

TABLE 9*b*.—AIR AT VARIOUS TEMPERATURES

Pressure	Pressure-volume product at				
	0°	50°	100°	150°	200°
0.76	1.0002	1.1838	1.3674	1.5508	1.7342
1	1.0000	1.1838	1.3674	1.5509	1.7344
5	0.9969	1.1830	1.3682	1.5525	1.7369
10	0.9934	1.1823	1.3693	1.5549	1.7403
15	0.9901	1.1818	1.3707	1.5578	1.7440
20	0.9870	1.1816	1.3724	1.5609	1.7480
25	0.9842	1.1816	1.3742	1.5641	1.7522
30	0.9817	1.1818	1.3762	1.5674	1.7565
35	0.9793	1.1822	1.3783	1.5708	1.7608
40	0.9773	1.1827	1.3806	1.5742	1.7651
45	0.9755	1.1833	1.3829	1.5777	1.7695
50	0.9740	1.1842	1.3854	1.5813	1.7739
55	0.9728	1.1852	1.3880	1.5849	1.7785
60	0.9720	1.1864	1.3908	1.5887	1.7831
65	0.9714	1.1880	1.3938	1.5927	1.7878
70	0.9712	1.1898	1.3970	1.5969	1.7927
75	0.9712	1.1918	1.4003	1.6013	1.7977

TABLE 9*c*.—HELIUM AT VARIOUS TEMPERATURES

Pressure, meters of mercury	Pressure-volume product at		
	0°	50°	100°
0.76	0.9998	1.1827	1.3657
1	1.0000	1.1829	1.3659
5	1.0028	1.1856	1.3685
10	1.0062	1.1890	1.3718
15	1.0097	1.1923	1.3751
20	1.8132	1.1957	1.3784
25	1.0167	1.1990	1.3816
30	1.0202	1.2024	1.3849
35	1.0236	1.2057	1.3882
40	1.0271	1.2091	1.3915

These data present what is perhaps the better side of the case. When gases with more complex molecules are concerned, or when the temperature of observation is close to the point at which condensation takes place, the deviations from Boyle's law become quite large. Some data[1] for such substances will be found on page 61 in connection with methods of allowing for these deviations in certain calculations. Thus when at 0° the pressure of carbon dioxide is actually 26.7 atmospheres the value to be expected from the constancy of the pressure-volume product is 29.4, which is in error by over 10 per cent. Similarly ether vapor at 220° has a calculated pressure-volume product which is 33 per cent in error when the pressure is 30 atmospheres. Hence some judgment is required in the application of Boyle's law, as is the case for the other gas laws about to be stated. But the law is true to within 1 or 2 per cent for most permanent gases under pressures up to about 10 atmospheres, at ordinary or high temperatures.

Law of Gay Lussac.—When a quantity of gas at 0°C. is heated while the volume is kept constant, the pressure increases a definite fraction of its value at 0° for each degree rise in temperature. This fraction is 0.003667, or 1/273 of the pressure at 0°. For example, if the original pressure at 0° were 1 atmosphere, it would be 1.003667 at 1°, 1.03367 at 10°, 1.3667 at 100°. Since this fractional increase per degree is 1/273, the pressure would reach 2 atmospheres at 273°. If the temperature were reduced until the pressure was ½ atmosphere, this temperature would be $\frac{273}{2}$ degrees below zero. Thus at any temperature t the pressure is $\frac{273 + t}{273}$ times the pressure at 0°C.

Scale of Temperature.—By choosing as a temperature scale one composed of Centigrade degrees, with 273 as the melting point of ice (Centigrade zero), we would have a scale such that the pressure of a gas at constant volume is proportional to the temperature. For if the pressure is unity at 0°C. where the newly chosen temperature is 273, and it increases 1/273 of this pressure for every degree rise in temperature, it would be 2 atmospheres at 273°C., and this temperature on the new scale is 273 + 273, or double the temperature corresponding to 0°C. This may be called a gas-scale of temperatures; it is more often called the absolute scale or Kelvin temperature scale after the physicist of that name. There are reasons other than the temperature coefficient of expansion of gases for believing that −273°C. is an

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[1] Data for other substances may be found in the Landolt-Bornstein Tables; in the Communications of the Physical Laboratory of the University of Leiden in Holland (available in English); and in the tables published by the Smithsonian Institution.

TABLE 10.—CHANGE OF PRESSURE-VOLUME PRODUCT OF HELIUM WITH TEMPERATURE[1]

A quantity of helium which at 0°C. and 1 atmosphere pressure was 1,000 c.c. was subjected to various temperatures and pressures. Under *pv* are the observed pressures multiplied by the observed volumes. From these products and the weight of helium employed, 0.17850 gram, the value of pv/T for a mol of helium has been calculated and is shown in the last column. If the ideal gas law described accurately the behavior of helium, all of these values would be 82.07. The deviations are not due to experimental errors in the measurements; they show real deviations of the gas laws.

Temperature Centigrade	T absolute	Pressure in atmospheres	pv	$\frac{pv_m}{T}$
100.3	373.3	42.574	1387.25	83.2
		54.459	1393.14	83.5
		66.590	1399.29	83.9
20	293	27.539	1086.64	83.0
		36.303	1090.28	83.2
		53.708	1099.18	83.9
0	273	1.000	1000.00	82.0
		26.634	1013.92	83.0
		38.565	1018.50	83.5
		50.240	1025.21	84.1
−103.6	169.5	20.580	631.35	83.2
		24.100	632.96	83.5
		29.185	635.97	83.7
		33.383	638.45	84.1
−182.8	90.3	13.751	337.87	83.7
		16.019	338.98	83.9
		18.189	340.25	84.1
−216.56	56.5	9.564	211.32	83.7
		10.502	211.71	83.9
		11.448	212.19	83.9

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[1] Onnes, *Comm. Phys. Lab. Univ. Leiden*, **102a**, (1907).

"absolute zero" of temperature below which it is impossible to go by any means whatever. Some of these reasons will be given later in their proper place. It will be sufficient to consider that absolute temperatures are gas-scale temperatures; that is, temperatures such that the pressure-volume product for a quantity of gas is proportional to the temperature. This law, like Boyle's law, is not strictly true for gases at low temperatures (where condensation is possible) or at very high pressures, but it is the limiting law which describes the behavior of gases more and more closely as higher temperatures and lower pressures are employed. An example of actual experimental results is given in Table 10. To change Centigrade temperatures to absolute temperatures, add 273° to them[1]. In this book the usual custom of denoting these temperatures is followed, Centigrade temperatures by t, absolute temperatures by T. Thus $T = (273 + t)$ in every case.

Gas Thermometer.—Since the increase of the pv product is proportional to the absolute temperature for an ideal gas, and nearly so for an actual gas, a thermometer may be constructed on this principle. If a quantity of gas at constant volume has a pressure p_0 in melting ice, a pressure p_{100} when surrounded by water boiling at 1 atmosphere, and a pressure p_t at some unknown temperature t, then this temperature may be determined from the equation[2]

$$t = \frac{100(p_t - p_0)}{p_{100} - p_0} \tag{1a}$$

This expression is the quotient of $(p_t - p_0)$, the actual increase, and $(p_{100} - p_0)/100$, the increase of pressure per degree. That is, $(p_t - p_0)/(p_{100} - p_0)$ is the fraction of the increase per hundred degrees, and 100 times this fractional increase is the increase in temperature in degrees.

A corresponding set of measurements of the volume of a quantity of gas at constant pressure at the two standard temperature points and at an unknown temperature t leads to the expression

$$t = 100\,\frac{v_t - v_0}{v_{100} - v_0} \tag{1b}$$

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[1] More exactly, 273.09°. Dushman, *General Elec. Rev.*, Feb., 1915. Keyes, *J. Am. Chem. Soc.*, **42**, 54 (1920), summarizes the researches conducted to determine this figure, and gives 273.14°.

[2] Buckingham, *Bull. Bureau Standards*, **3**, 237 (1907).

Except in work of the greatest precision, the deviations of these scales from true temperatures are not important when the gas employed obeys Boyle's law approximately. On the absolute scale we may write

$$\frac{T}{T_0} = \frac{v}{v_0}\ (p = \text{constant}) \quad \text{or} \quad \frac{T}{T_0} = \frac{p}{p_0}\ (v = \text{constant}). \qquad (1c)$$

These scales are known respectively as the constant pressure gas scale and the constant volume gas scale. They both give true absolute temperatures to within very small fractions of a degree. It should be noted that equation (1*c*) is true only if the expansion per degree is 1/273 of the volume at zero. This is not the case in equation (1*a*); here it is only necessary that the temperature coefficient of pressure increase at constant volume is the same throughout the temperature range 0 to 100°C.; that is, it is only necessary that $\frac{dp}{dt}$ = a constant; or, using the integral of this expression, it is necessary that $p = kt + a$; equation (1*c*) requires that a is $273k$. For example, a gas which is not an ideal gas, but which is described by van der Waals' equation, to be given later, will give correct Centigrade temperatures when equation (1*a*) is employed, but will not lead to correct absolute temperatures as shown in equation (1*c*).

Ideal Gas Law.—By combining the two laws just given we obtain the equation

$$\frac{pv}{T} = \text{const.},$$

where the numerical value of the constant depends on the units chosen for expressing p and v and on the quantity of gas under consideration. If we consider a "mol" of gas (*i.e.*, the molecular weight of it in grams) as the standard quantity, then the numerical value of the constant in a given set of units is independent of the nature of the gas, and is usually denoted by R. The equation then becomes, for one mol of any gas,

$$pv = RT \qquad (2)$$

A *mol* of gas (or gram-molecular weight) is chosen as a unit in preference to a gram, since the molecular weight of any gas occupies the same volume as the molecular weight of any other gas. Then from the known value of the constant R which applies to all gases we may calculate the pressure or volume of a mol of any gas.

Since the volume of n mols of gas is obviously n times as great as the volume of one mol, the equation may be written so as to describe the behavior of any quantity of gas in terms of the one constant R,

$$pv = nRT \tag{3}$$

where n is the number of molecular weights or mols of gas under consideration.

The numerical value of R depends only on the units chosen to express p and v. It should be noted that R has the dimensions of work, since the product pv is force per unit area × volume, or force × distance; and the quantities n and T are numbers. Suppose a cylinder of area a, fitted with a tight piston. When this piston moves through a distance h against a pressure of p on each square centimeter of the piston, the force exerted is pa, and it acts through the distance h; but since ah is the volume of the cylinder, pah is pv, and this has the dimensions of work.

Let us express p in dynes per square centimeter and v in cubic centimeters; and calculate the value of R from the density of oxygen. Morley[1] found that a liter of this gas at 0° and 76.0 cm. of mercury pressure weighed 1.4290. Since the density of mercury is 13.60, the mass of the column of mercury supported on a square centimeter of gaseous surface is 13.60 × 76.0, and the force is the product of mass and the acceleration of gravity, or 13.60 × 76.0 × 980 = 1,013,300 dynes per square centimeter. The value of n is 1.4290/32.00 = 0.0446 mols. Substituting in (3) we have

$$\begin{array}{ccccccccc} 1{,}013{,}300 & \times & 1000 & = & 0.0446 & \times & R & \times & 273 \\ p & & v & = & n & & R & & T \end{array}$$

whence

$$R = 8.316 \times 10^7 \text{ ergs} = 8.316 \text{ joules.}$$

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[1] *Smithsonian Contr. Knowledge*, **29**, 1–117 (1895).

If we wish to keep R in terms of the cubic centimeter and atmosphere, then, using the same data

$$1.00 \times 1000 = 0.0446 \times R \times 273$$

and $R = 82.07$ c.c.-atmospheres[1] or 0.08207 liter-atmospheres. In later calculations it will be convenient to have the value of R expressed in heat units, calories. Since one calorie is 4.182 joules, $R = 8.316/4.182 = 1.99$ calories.

Equation (3) describes the behavior of most gases under wide variations in pressure and temperature with an accuracy of about 1 or 2 per cent. An **"ideal gas"** is one whose behavior would be exactly in accordance with this equation. No such substance is known, but all actual gases approach the condition of the ideal gas more closely as the pressure upon them decreases and as the temperature increases. The "ideal gas" is thus the limiting condition for all gases, and equation (3) is called the ideal gas law or ideal gas equation. The term "perfect gas" is also commonly employed in this connection, but "ideal" serves to keep constantly before us the imaginary character of such a substance. In a later section (page 57) we shall consider gases under conditions of high pressure and at temperatures near the condensation point, where the ideal gas laws do not apply even roughly in some cases. But for calculations at ordinary temperatures and moderate pressures (up to 10 atmospheres for example) the deviations of ordinary gases from the equation $pv = nRT$ are commonly less than 2 per cent.

Mol Fraction.—A common method of expressing the composition of a mixture is in terms of the number of mols of a substance present, divided by the total number of mols of all substances present. As an example, the composition of the earth's atmosphere may be computed in terms of the mol fractions of the constituents. Analysis shows that 100 grams of air contain 23.25 grams of oxygen, 75.5 grams of nitrogen and 1.24 grams of argon. On dividing each of these weights by the molecular weight of the substance in question we find 0.727 mols of oxygen, 2.70 mols of nitrogen and 0.032 mols of argon, total mols 3.459 in

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[1] A cubic-centimeter-atmosphere is the work necessary to move a piston of one square centimeter area through a distance of one centimeter against a pressure of one atmosphere. One small calorie is equivalent to 41.24 c.c.-atmospheres.

100 grams of air. The mol fraction of oxygen is therefore $\frac{0.727}{3.459} = 0.210$, that of nitrogen is $\frac{2.70}{3.459} = 0.781$, and that of argon is $\frac{0.032}{3.459} = 0.009$.

At 20° and 1 atmosphere pressure the volume of 32 grams of oxygen is 24 liters. By mixing 5,050 c.c. of oxygen, 18,800 c.c. of nitrogen and 150 c.c. of argon, a total volume of 24,000 c.c. is obtained and the mixture has properties identical with those of air. The mixture contains 0.210 mols of oxygen, 0.781 mols of nitrogen and 0.009 mols of argon, therefore a total of 1 mol. We may thus properly speak of this 24 liters of air as a mol of air, though it contains less than a mol of any one substance. A mol of a gaseous mixture is that quantity of it which occupies the same volume as 32 grams of oxygen under the same conditions of temperature and pressure. This quantity of gas would of course condense to a mol of liquid mixture. By multiplying the number of mols of each substance in a mol of air by its molecular weight and adding, we find that a mol of air weighs 29.00 grams. This "molecular weight of air" is useful in applying the simple gas laws to air, and in calculating molecular weights of gases from the densities expressed as multiples of the density of air under the same conditions. For example, refer to the description of molecular weight determinations by the method of Victor Meyer, page 42.

Dalton's Law.—This law states that in a mixture of gases each exerts its pressure independently of the others, or in other words the "partial pressure" of one gas is unaltered by the presence of another gas which also exerts a pressure. By partial pressure we mean that part of the total pressure due to the particular species of molecule under consideration. Obviously the total pressure in any gaseous mixture must be the sum of the partial pressures of all the gaseous substances present. Suppose the three bulbs *A*, *B*, and *C*, of Fig. 4 to be of equal volume and filled with oxygen, nitrogen and hydrogen, each under a pressure of 1 atmosphere. If the stop-cock *a* is opened and the nitrogen is forced from *B* into *A* (by flowing mercury into *B*) the total pressure in *A* should rise to the sum of the two partial pressures; $p_O + p_N$. According to Dalton's law the pressure exerted by oxygen on the walls of vessel *A* is still 1 atmosphere, or the same as its pressure when it was alone in the vessel. The law further requires that the partial pressure of the nitrogen be 1 atmosphere, since it is in a vessel of the same size as formerly. Direct experiment shows that the total pressure is indeed very close to 2 atmospheres as required by the law. If the hydrogen be similarly forced into vessel *A* the total pressure rises to 3 atmospheres; *i.e.*, $p_O + p_N + p_H = 3$.

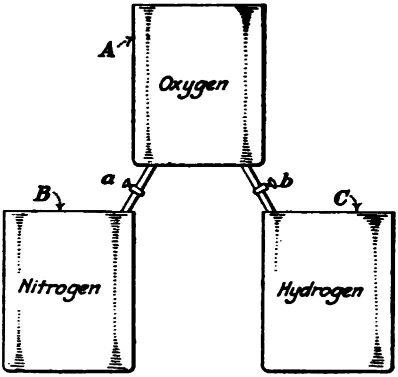

FIG. 4.

The following table[1] shows the percentage increase in volume

TABLE 11

Column 1 gives the volume of the gas first written at the head of each succeeding column in 100 c.c. of mixture. The other columns show the percentage increase in volume due to mixing, when the total pressure is kept at 1 atmosphere. As an illustration, when 20 c.c. of carbon dioxide and 80 c.c. of nitrogen are mixed, the resulting total volume is 101.96 c.c. but when 80 c.c. of carbon dioxide and 20 c.c. of nitrogen are mixed, the total volume is 101.46 c.c.

Volume per cent of first gas	Per cent increase in volume on mixing at 20°					
	$N_2O + N_2$	$CO_2 + N_2$	$N_2 + O_2$	$N_2O + CO_2$	$N_2O + O_2$	$CO_2 + O_2$
10	1.07	1.02	0.37	0.38	0.96	0.98
20	2.14	1.96	0.79	0.85	1.78	1.53
30	2.86	2.49	1.07	1.17	2.51	2.01
40	3.16	2.72	1.21	1.34	2.88	2.34
50	3.06	2.61	1.27	1.42	3.03	2.41
60	2.81	2.41	1.11	1.17	2.70	2.20
70	2.34	2.00	0.89	1.02	2.11	1.88
80	1.79	1.46	0.61	0.64	1.43	1.33
90	0.97	0.81	0.34	0.41	0.85	0.71

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[1] P. Fuchs, *Z. physik. Chem.*, **92**, 641 (1918).

when gases at 1 atmosphere pressure are mixed in varying quantities and the total pressure is kept at 1 atmosphere. All of the figures should be zero if Dalton's law were exact. It will be noticed that the deviations are all of the order of 1 or 2 per cent, as with the other simple laws stated above.

While it is difficult to state general rules, it will be observed that the volume changes are larger the more the components differ from one another in physical properties, (such as condensation point) and in chemical structure. The maximum deviations occur in the presence of an excess of the gas with the lower critical temperature (page 78) in the mixture. When the gases approach each other in physical properties the maximum deviation from Dalton's law occurs in the 1:1 mixture; this is not true when the components differ considerably.

It has been possible in some cases[1] to find materials which allow the free passage of the molecules of one gas but not of other gases, and thus to measure partial pressures directly. The arrangement of the apparatus is shown in Fig. 5. The porcelain vessel *A* contains a platinum tube *B* sealed to a procelain tube connected to the pressure gage *b*. The apparatus, except the gages, is enclosed in an electric furnace which maintains a high temperature. When hydrogen is introduced through the inlet pipe *c* gages *a* and *b* record the same pressure, since the platinum tube does not retain hydrogen molecules at a high temperature, but allows them free passage. If nitrogen is introduced through the *c* inlet, gage *a* shows an increase in pressure, since it records the total pressure of all gases present. But the platinum tube does not allow nitrogen to pass, and gage *b* still records only hydrogen pressure. It is found by experiment that the introduction of nitrogen does not change the reading of gage *b*, which shows that the pressure of hydrogen in *A* is

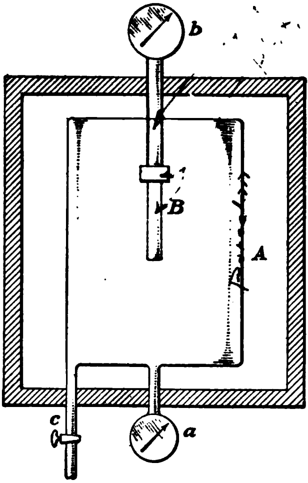

Fig. 5.

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[1] Lohnstein, *Z. physik. Chem.*, **54**, 715 (1906).

unchanged by the introduction of nitrogen. The differences between the readings of the two gages is of course the partial pressure of the nitrogen, and this is also found to agree with that demanded by Dalton's law.

Dalton's law may also be stated as follows: The partial pressure of any gas in a mixture of gases is proportional to the mol fraction of that gas. If p is the total pressure on a mixture of several components, a, b, c . . . x - mol [illegible]

$$p_a = px_a;\ p_b = px_b;\ p_c = px_c\ .\ .\ . \tag{4}$$

From this relation the mol fraction may be calculated if the partial pressure is known, or the partial pressure may be computed from a mol fraction determined by analysis. These calculations will be made frequently in the chapter on chemical equilibrium.

Avogadro's Law.—The number of molecules contained in a given volume of gas under any fixed conditions of temperature and pressure is independent of the nature of the gas. A more common statement of the law is that equal volumes of all gases under standard conditions of temperature and pressure contain the same number of molecules; but it should be made clear that so long as the two gases compared are at the *same* temperature and pressure, it is immaterial what the actual conditions are. The truth of this proposition was not conceded for a long time after it was put forth, and until recently its main support was the fact that the volumes of gases entering chemical reactions were simple whole multiples of each other and of the gaseous product formed. For example, since a volume of hydrogen and one of chlorine unite to form two volumes of hydrogen chloride without excess of either constituent remaining, it follows that the volume of hydrogen contained just the same number of particles as the volume of chlorine, or else just twice as many or half as many. Further, the number of molecules of hydrogen chloride is equal to the sum of the numbers of hydrogen molecules and chlorine molecules, for there are two volumes of gas after the reaction just as there were two volumes before it. Since no substance has ever been prepared which contained less chlorine per molecular weight than hydrogen chloride it is natural to conclude that there is only a single atom of chlorine in each molecule of hydrogen chlorine. The same statement holds for hydrogen. So it seems safe to state that the volume of chlorine contains exactly the same number of molecules as the volume of hydrogen. It follows also that the molecules of each of these substances contain two atoms, for the molecules of hydrogen chloride all contain hydrogen and there are twice as many of them as there were molecules of hydrogen used in their formation.

It has been shown by careful experiments that two volumes of hydrogen and one of oxygen form two volumes of water vapor. Avogadro's law states that the number of particles of water vapor formed is twice as great as the number of molecules of oxygen used, hence the oxygen molecule also contains two atoms. While definite conclusions should not be drawn from a single set of experimental facts such as these, the facts here stated are supported by all reactions in which oxygen gas takes part.

Avogadro's Number.—Within the last 10 years experiments have been made (some of which will be mentioned later in their proper place) from which it is possible to calculate the number of molecules in a gram-molecule. The experiments have been made by numerous investigators, using a variety of methods based on widely different phenomena, but among all of them the agreement is excellent. Each of the methods has been subjected to searching tests and it may be said with absolute conviction that the numbers found are true, in spite of the inconceivably large value of them. It would of course be quite impossible for any set of experimenters to count such numbers in a life time, but fortunately this has not been found necessary. All of the determinations are of the order of 6×10^{23}, or 600,000,000,000,000,000,000,000, and the molal volume of all gases contains this number of molecules.

In the following table are given some of the more recent determinations of this number, commonly called "Avogadro's number," or Avogadro's constant. A review of the experimental methods on which these determinations are based would be beyond the scope of this book, since the experimental procedures are usually complex, and the calculations in connection with them are somewhat involved. There is an agreement among them which would be gratifying if the same method had been used by all the observers; when it is considered that the determinations have been made by methods which are quite different in principle, to say nothing of the apparatus used, the concordance is truly remarkable and convincing.

TABLE 12.—AVOGADRO'S NUMBER[1]

The table shows the number of molecules in a gram molecule as determined by the method noted.

Observer	Method	Molecules per gram. molecule
	Mean free path of a molecule	5 to 6 × 10^{23}
Perrin..........	Brownian movement of colloids	6.8
Svedberg........	Intensity of Brownian motion	6.2
Brillouin........	Intensity of Brownian motion	6.9
Fletcher........	Rate of fall of oil drops in air	6.03
King[2]...........	Scattering of solar radiation	6.2
Pacini[3].........	Scattering of solar radiation	5.7
Rutherford......	Charge on an alpha particle	6.0
Millikan........	Determination of unit electric charge	6.06 ± 0.01
Planck..........	Radiation laws	6.06
Perrin..........	Angular displacement of a colloidal particle	6.5
Boltwood.......	Alpha particles in helium from radium	6.3
Curie...........	Alpha particles from polonium	6.5
Rutherford......	Kinetic energy of an alpha particle	6.2
Westgren[4]......	Change of distribution of colloidal particles	6.09

Among these determinations that of Millikan is perhaps the most accurate, and it may be said with certainty that we know the "population" of a gram-molecule as accurately as we know that of any large city. Probably no human mind is able to grasp the meaning of such an exceedingly large number as this, but a clear concept of its size is fortunately not required in order to benefit from the truth of Avogadro's law. The actual determination of the number is important to us chiefly as real tangible proof of the law. Indeed the table shows such agreement among the experiments quoted (which are by no means all of the researches made in this field, but only selected examples) as to leave little doubt of the validity of the law. The actual determination of the number was accomplished just a hundred years after the first statement of the law (1811) by Avogadro.

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[1] References to the original articles dealing with these experiments, together with a brief description of some of them, will be found in the *General Electric Review*, **18**, 1159 (1915).

[2] *Trans. Roy. Soc. Canada*, **8**, 59 (1914).

[3] *Nuovo Cimento*, **10**, 131 (1915).

[4] *Arkiv. Mat. Astron. och Fysik*, **13**, 14 (1918).

Viewed in the light of this number the attainment of a "vacuum" seems quite hopeless, for the lowest pressures ever observed, after the most efficient removal of gas from a container are about 0.001 dyne per square centimeter (this is less than $1/100,000,000$ of an atmosphere), and in this "vacuum" the number of molecules per cubic centimeter is greater than the population of the earth.

Molecular Weight Determinations—Dumas Method.—When the ideal gas equation is written $pv = \frac{m}{M} RT$, it will be seen that the molecular weight of a gas may be determined when the weight of a known volume at some definite temperature is known. Of the many experimental procedures for molecular weights, that of Dumas is perhaps the best known, and most simple. It consists in immersing a weighed bulb with a small neck in a bath of boiling water while a quantity of liquid within the bulb boils until all air is expelled, and there is no excess of liquid remaining. (For liquids boiling higher than water, an oil bath may be used.) The bulb is then sealed quickly, and the barometer is read. At the moment of sealing, there is in the bulb vapor at the barometric pressure and at the temperature of the bath. Thus T and p are known, m is determined by weighing the bulb, and v by filling the bulb with water and weighing again. As the bulb when first weighed is filled with air which is expelled by the boiling liquid, it is necessary to compute the weight of air expelled and subtract it from the first weighing in order to obtain the weight of the empty bulb alone. Commonly a bulb of about 500 c.c. is used. As it is difficult to weigh this bulb accurately, a modified procedure has been devised as follows:[1] A quantity of the liquid whose vapor is under examination is placed in a glass vessel of the form shown in Fig. 6, and this bulb is heated in a bath of constant known temperature until the excess of liquid is expelled; the bulb is then sealed at *c* and removed from the bath. Now the small bulb *a* is immersed in liquid air, while the large one is heated, until all of the substance is condensed into the tiny bulb. This is then sealed off and weighed, emptied and weighed again, thus giving the weight of vapor present at the temperature *T* and pressure of the atmosphere at the time of sealing. The large bulb is weighed roughly, its tip is broken off under water, which then completely fills the bulb, and it is weighed again to about a tenth of a gram. This difference in weight gives the volume of the large bulb, to which is added that of the tiny bulb (less than 3 c.c.), also determined by filling with water. Some results obtained in this way are shown below.

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[1] Schultze, *Physikalische Ztsch.*, **14**, 922 (1914).

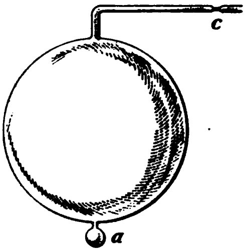

FIG. 6.

TABLE 13.—MOLECULAR WEIGHTS BY DUMAS METHOD

Substance	Temperature	Weight of a liter of vapor	Molecular weight found by experiment	Formula weight
Ether	70°	2.634	74.15	74.08
Ether	80°	2.560	74.13	74.08
Ether	90°	2.485	74.03	74.08
Carbon disulfide	80°	2.687	77.84	76.14
Acetone	80°	2.010	58.22	58.05
Benzene	95°	2.583	78.01	78.05
Chloroform	95°	3.986	120.40	119.40
Alcohol	95°	1.522	45.97	46.05
Methyl alcohol	95°	1.065	32.17	32.03
Hexane	95°	2.853	86.15	86.11
Ethyl acetate	95°	2.919	88.16	88.06
Nitrobenzene	250°	2.882	123.70	123.10

The divergences between experimentally measured molecular weights and those calculated from the formula of the substance are not due to errors in the experiments themselves, but to a failure of the ideal gas equation to describe accurately the behavior of the vapor. Such deviations can be eliminated from this method to a large extent by the "limiting density" procedure mentioned in the previous chapter.

Victor Meyer's Method.—This procedure is adapted to substances which vaporize at somewhat higher temperatures than those suited to Dumas' method; indeed it can be applied at all temperatures below the softening point of glass. In principle the method consists in dropping a weighed quantity of the liquid or solid substance into a vessel filled with hot air at such a temperature that the substance vaporizes readily. The hot bulb is made much larger than the volume which the substance will occupy as a vapor, and since a constant pressure is maintained in the bulb, a volume of air equal to that of the vapor

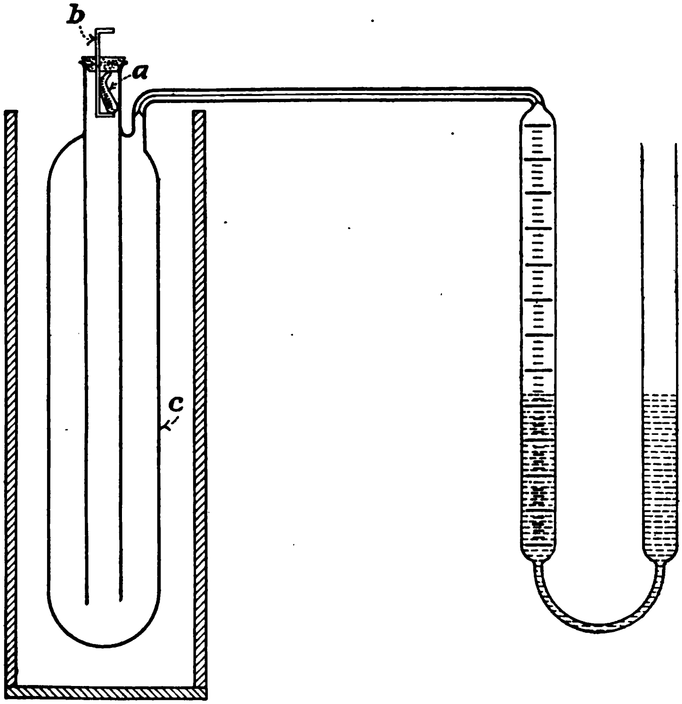

Fig. 7.—Victor Meyer apparatus.

formed is expelled into a measuring vessel. That is, a vapor has been substituted for an equal volume of air for convenience in measuring.

One form of Victor Meyer apparatus is shown in Fig. 7. The substance whose molecular weight is desired is weighed in a little bulb *a*, which has a capillary stem, and is supported on the rod *b* so that a turn of the rod releases it. The bulb falls into the heated portion of the vaporizing chamber *c*, where the substance evaporates, and displaces an equal volume of air from the top of the chamber. This air is collected in the buret and measured. It represents the volume which the vaporized substance would have at the temperature of the buret if it were a gas at this temperature. Knowing the barometric pressure and the temperature in the buret, we have all of the necessary data for substituting in the equation $pv = (m/M)\,RT$, and the molecular weight M is readily calculated. The temperature used in this calculation is that of the gas in the buret, not the temperature of the vaporizing chamber; for the vaporized substance has displaced a volume of hot air equal to its volume while hot, and this air has been cooled for convenience in measurement. Some typical results are shown in Table 14.

TABLE 14.—MOLECULAR WEIGHTS OBTAINED BY THE VICTOR MEYER METHOD[1]

Bromine, formula weight 159.8

Weight taken	0.1970	0.2015	0.1475	0.2059	0.1861
Vol. air displaced	30.33	30.15	22.71	31.05	29.00
Buret temperature (abs.)	297	298	296	298	298
Pressure (corr. for aqueous tension in the buret)	735	735	735	755	729
Mol. wt. calcd	164	164	163	167	164

	Alcohol, formula weight 46.05			Ether, formula weight 74.1		
Weight taken	0.0494	0.0612	0.0561	0.1023	0.1159	0.0971
Volume air displaced	27.23	33.68	30.54	35.33	40.40	33.68
Buret temperature (abs.)	297	297	297	306	307	305
Pressure (corr.)	725	725	725	733	733	733
Mol. wt. calcd	45.9	46.4	46.4	75.7	75.3	74.9

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[1] MacInnes and Kreiling, *J. Am. Chem. Soc.*, **39**, 2,350 (1917).

The experimental results are uniformly higher than the accepted values which accord with the simple molecular formula. This is to be expected since all of the substances have large molecules, the vapors in the heated bulb are at pressures which are not far removed from the condensation pressures, and the molecular weights were calculated from the simple gas laws. If the results are calculated from the van der Waals equation (for example) they will be found much closer to the accepted formula weights. That is, the differences are due to the failure of the law of ideal gases to describe accurately the behavior of the vapor.

KINETIC THEORY OF GASES

Fundamental Equation.—The molecules of a gas are not at rest, but move about through the confining space with great rapidity,[1] colliding frequently with each other and with the walls of the vessel surrounding them. This statement is supported by the fact that when two gases are brought in contact and the mixture is allowed to stand, it finally becomes homogeneous or of uniform composition throughout. If a quantity of chlorine be placed in the bottom of a vessel by displacing part of the air in it, a distinctly greenish layer will be seen. If this is allowed to stand for some time the green layer diffuses throughout the whole vessel, and, there is no longer any visible boundary between the two gases. This mixing is not dependent on any stirring, it will take place if the vessel is kept absolutely quiet and at a constant temperature.

The pressure exerted on the walls of a container by a gas is entirely due to collisions which take place between the moving molecules and the walls. It is known that the pressure does not decrease if a gas is allowed to stand indefinitely in a closed space at constant temperature, and that a gas does not continuously absorb heat from the surroundings to supply the energy of motion of its molecules. This can be true only if the molecules are perfectly elastic as regards their collisions with one another, for otherwise the collisions would absorb energy and the intensity of motion would gradually decrease; and cause the pressure

[1] The molecules in air move at about a half mile per second, but the average straight line distance travelled between collisions is only about 0.0001 m.m., thus making the number of hits per second for each molecule about five thousand million.

to fall off. The pressure is perfectly constant on all the walls at all times, so the bombardment of the walls must be uniformly distributed.

Within a gas the molecules move about in the utmost chaos, with no regularity whatever, and at widely different velocities. A molecule which has a high velocity at one instant may suffer a collision which changes its direction and velocity at any moment. Indeed the path of each molecule is absolutely haphazard, and the state of a gas must be thought of as absolute confusion. But it is convenient in visualizing the behavior of molecules, as regards pressure exerted on the surrounding walls, to consider their motions along three axes perpendicular to the faces of a confining cube; and to consider the average velocity of all the molecules, in place of the rapidly changing velocity of a single molecule.

Let us consider that the molecules, in place of moving about in chaos, move in three directions perpendicular to the faces of a cube, and that one-third of them move in each of the directions at any moment of time. This is equivalent to resolving the actual motions into their components along three perpendicular axes and considering the motion in one direction at a time. Let m be the mass of a single molecule moving in one direction with a velocity u_1 centimeters per second, and let the side of a cube containing the gas be l. In order for a molecule to make a complete round trip from a given point to one wall, then to the other wall and back to the starting point, it must travel the distance $2l$, which will require $\frac{2l}{u_1}$ seconds. To state this in another way, the molecule will make $\frac{u_1}{2l}$ round trips per second, and hence strike a given wall of the vessel $\frac{u_1}{2l}$ times per second. This molecule approaches a wall with velocity u_1 before the collision, and after its collision the velocity is $-u_1$. Its momentum is then changed from mu_1 to $-mu_1$, and this takes place at a wall every time a molecule strikes this wall.

The total change in momentum of this molecule at a given wall per second is therefore $2mu_1 \times \frac{u_1}{2l}$. Now let n be the number of molecules in the cube, and let u be the average velocity. We have already assumed that one third of the molecules moved in each of the three directions. The change in momentum per second at one wall of the cube for each of the $\frac{n}{3}$ molecules striking it will be

$$2mu \times \frac{u}{2l} \times \frac{n}{3} = f$$

or $\frac{mu^2}{l}$ for each of the $\frac{n}{3}$ molecules. The force f exerted on a wall is the rate at which momentum is imparted to it,[1] so this expression is equal to the force exerted by the gas on a wall of the cube. Pressure is by definition the force exerted upon a unit area and the area of the wall is l^2, whence

$$p = \frac{f}{l^2} = \frac{1}{l^2} \times 2mu \times \frac{u}{2l} \times \frac{n}{3} = \frac{1}{3}\,\frac{mnu^2}{l^3} \tag{5}$$

But l^3 is the volume of the cube, which we will call v, and our equation then becomes

$$p = \tfrac{1}{3}\,\frac{mnu^2}{v} \tag{6}$$

Since for a mol of gas pv is equal to RT (equation 3) we may write

$$pv = \tfrac{1}{3}mnu^2 = RT, \tag{7}$$

which is the fundamental equation of the simple kinetic theory. If p is in dynes per square centimeter (bars), v is in cubic centimeters, m in grams and u in centimeters per second, R has the value 83.2×10^6 ergs; and n is Avogadro's number.

Validity of the Equation.—In deriving this equation we have assumed that the molecules of a gas move perpendicular to the faces of a cube with an average velocity u, whereas they move about in inconceivable confusion and strike the walls at all possible angles and with velocities varying from zero to very high values. Ordered motion could not possibly be established in the three directions and (owing to collisions) would not remain ordered for a finite length of time if established. Hence a reasonable suspicion of the validity of the equation thus derived may exist, and it must justify its existence by according with the known behavior of gases or be valueless. Let us examine the case for and against our equation.

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[1] Force has the dimensions, $\frac{ml}{t^2}$, and momentum is $\frac{ml}{t}$, hence $\frac{ml}{t} \times \frac{1}{t}$ is the rate of imparting momentum to a surface.

In perfect random motion among a very large number of molecules, with millions of millions of collisions taking place, the same number of impacts would probably fall on each face of the cube in a given time, and among such a large number of perfectly random hits, they would probably be distributed about uniformly over the area; our assumption was an equal number of collisions on each wall, uniformly distributed over it. If we resolved the motion of each molecule in the totally chaotic state along three perpendicular axes at any given instant of time, we would probably find the same average velocity resolved on each axis, otherwise the pressure exerted on the different walls would not be the same, and this is contrary to experimental evidence. Our assumption is that equal velocities are resolved along each axis.

If we write equation (7) in the form

$$\tfrac{2}{3}n \times \tfrac{1}{2}mu^2 = RT$$

we see that the kinetic energy of a molecule, $\frac{1}{2}mu^2$, must be directly proportional to the absolute temperature T, and that, since nothing has been assumed as to the kind of molecule concerned, the equation requires the kinetic energy of all molecules at a given temperature to be the same, since RT for a molecular weight of all gases has the same value. This statement requires that when two gases at the same pressure and temperature are mixed in any proportion there be no change of temperature. For in such a mixture the kinetic energies of all the molecules would speedily become the same at equilibrium. And if they were not the same before mixing, the change of kinetic energy should cause a change in temperature, since $\frac{1}{2}mu^2$ for each molecular species is proportional to the absolute temperature. The experimental fact that there is no change in temperature on mixing gases is thus evidence for the validity of the equation derived. The loss of kinetic energy of one species might be compensated by the gain for another (and hence conceal any temperature change) for one mixture of two gases, but a mixture in some other proportions would reveal this compensation effect. As a matter of fact, no change in temperature is observed, whatever the relative quantities of gas employed.

Dalton's law of partial pressures is satisfied by the mixture, since there is no change of pressure and the total volume is the same as the sum of the volumes before mixing. Now a fixed number of molecules of one kind could not exert the partial pressure in the mixture required by Dalton's law (that is, the pressure which the gas would exert if it alone were present in the total volume) unless the kinetic energy of the molecules of this kind were unchanged by the process of mixing. Hence there is *no change of kinetic energy on mixing;* and the equation we have derived requires that there be none.

Rate of Effusion of Gases.—At any given temperature the kinetic energies of two kinds of molecules should be the same according to our equation, that is

$$\tfrac{1}{2}m_1u_1^2 = \tfrac{1}{2}m_2u_2^2$$

or

$$\frac{u_1}{u_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}, \tag{8}$$

since the masses of the molecules are proportional to the molecular weights M_1 and M_2, and to the densities d_1 and d_2. This equation states that the velocity of the molecules should be inversely proportional to the square root of the density of the gas. Since effusion through a small hole is a manifestation of molecular motion, the correctness of this equation may be tested by comparing the rates of effusion of gases through a given opening. The statement in equation (8) is in fact Graham's law of effusion of gases. Some of his data are here quoted to show that this consequence of the fundamental equation (7) is proved by experiment.

TABLE 15.—RATE OF EFFUSION OF GASES[1]

Gas	Density relative to air	Time of effusion relative to air	Square root of density	Velocity of effusion relative to air	Velocity calculated from square root of density
Air.....	1.0000	1.000	1.0000	1.000	1.000
Oxygen	1.1056	1.053	1.0515	0.950	0.951
N_2.....	0.9714	0.984	0.9856	1.016	1.015
CO.....	0.9678	0.987	0.9838	1.012	1.016
CH_4....	0.5549	0.765	0.7449	1.322	1.342
CO_2....	1.5290	1.218	1.2350	0.821	0.809
N_2O....	1.5290	1.199	1.2350	0.834	0.809

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[1] Graham, *Phil. Trans. Roy. Soc. London,* **136,** 573 (1846).

If the kinetic energy of a gas molecule depends only on its temperature and is a quantity independent of the nature of the gas.

$$pv = \tfrac{2}{3}\cdot\tfrac{1}{2}m_1u_1^2n_1 = \tfrac{2}{3}\cdot\tfrac{1}{2}m_2u_2^2n_2$$

If $p_1v_1 = p_2v_2$ at a given temperature the same volume of the two gases must contain the same number of molecules, *i.e.* $n_1 = n_2$, since $\tfrac{1}{2}m_1u_1^2 = \tfrac{1}{2}m_2u_2^2$, and this is the law of Avogadro.

Thus we see that our fundamental equation (7) is in substantial agreement with all the known facts concerning gaseous substances at moderate pressures, even though we have made rather broad assumptions in its derivation. Evidently these assumptions, while contrary to the mechanism of the processes occuring in a gas, lead to the same consequences as the actual operations taking place.

The equation may in fact be derived without assuming that the molecules have regular motion in given directions, and by taking into account the varied velocities shown at a given instant by the molecules, but such a derivation is beyond the scope of an elementary book. Students just beginning the study of physical chemistry will do well to concern themselves with the simpler derivation given above and the usefulness of the correct final equation (7) as an aid in forming a concept of the kinetic state of a gas, rather than to attempt a rigid derivation. They should perhaps view the "derivation" above as an attempt to make equation (7) appear plausible, and consider the agreement of deductions based on it (such as the specific heat equation for monatomic gases in the next section) with experimental facts as "proof" of its validity. Certainly the remarkable agreement between the derived specific heat values and those determined in a calorimeter constitutes a sufficient justification for the existence of the equation; and it will materially aid us in forming a conception of the nature of a gas.

Heat Capacity of a Monatomic Gas at Constant Volume.—The specific heat of a substance is by definition the ratio of the quantity of heat added to a gram of it to attendant rise in temperature. The molal heat capacity would then be the ratio of the heat absorbed by a molecular weight of it to the rise in temperature. If the substance is a monatomic gas which is not allowed to expand during the heating (and hence does no work against an external pressure), its molecular heat capacity may be calculated from equation (7). This calculation assumes that *all* of the energy added to a monatomic gas is used to increase the kinetic energy of the molecules; that none is used in producing rotation of the molecules or in any other way than in adding to the linear velocities of the molecules. It is for this reason that only monatomic substances are under consideration, for if 2 atoms are present in a molecule, energy is required to produce rotation of the atoms about axes perpendicular to the line joining their centers. Consequently in these substances the increase in kinetic energy of the molecules is not the only process absorbing heat. The derivation is as follows:

Let u_1 be the average velocity of the molecules at the absolute temperature T_1 and u_2 the average velocity at the higher temperature T_2 after the quantity of heat Q has been absorbed by a mol of the gas. The increase in kinetic energy of all the molecules is

$$\tfrac{1}{2}Nmu_2^2 - \tfrac{1}{2}Nmu_1^2,$$

where N is Avogadro's number of molecules in a mol of gas; and this increase in kinetic energy is equal to the heat added. Since we are concerned with a molecular weight of gas, the product Nm is equal to the molecular weight of the gas M. Writing the equation (7) for a molecular weight we obtain

$$p_1v = \tfrac{1}{3}Mu_1^2 = RT_1$$

and

$$p_2v = \tfrac{1}{3}Mu_2^2 = RT_2$$

By multiplying each of these equations by $\tfrac{3}{2}$ and subtracting the first from the second we obtain

$$\tfrac{1}{2}Mu_2^2 - \tfrac{1}{2}Mu_1^2 = \tfrac{3}{2}R(T_2 - T_1) \qquad (9)$$

as the difference between the kinetic energies of the molecules at the temperatures T_2 and T_1. This is therefore equal to Q, but Q is equal to the molal heat capacity of the gas, multiplied by the increase in temperature, that is $Q = C_v(T_2 - T_1)$, and, on substituting these quantities in equation (9) we have

$$Q = C_v(T_2 - T_1) = \tfrac{1}{2}M(u_1^2 - u_2^2) = \tfrac{3}{2}R(T_2 - T_1) \quad (10)$$

whence the molal heat capacity at constant volume is

$$C_v = \tfrac{3}{2}R = 2.98 \text{ cal. per degree.} \qquad (11)$$

Heat Capacity of a Monatomic Gas at Constant Pressure.—If the gas had been allowed to expand during heating, while the pressure was kept constant, work would have been done by the gas in pushing back the atmosphere, and a greater quantity of heat would have been required to produce the same increase of temperature. This additional quantity of heat absorbed and turned into work may be calculated as follows: The volume of the gas increases from v_1 to v_2 as a result of the increase of temperature from T_1 to T_2. Suppose the gas was in a cylinder of area *a* and volume v_1, and that during the heating the piston rose through the height *h* until the volume was v_2, as shown in Fig. 8. The piston has been raised through the height *h* against the pressure *p* exerted on each square centimeter of the piston. The work done is therefore force ($p \times a$) times the distance *h*, and, since *ah* is $v_2 - v_1$,

$$pah = W = p(v_2 - v_1) = R(T_2 - T_1)$$

since $pv_2 - pv_1$ is equal to $RT_2 - RT_1$ for a mol of gas. The value of *R* is 1.99 cal., hence the work done by a mol of gas in expanding against a constant pressure, when the expansion is due to a temperature change, is 1.99 cal. per degree. The gas absorbs heat equivalent to this work done, and this quantity of heat should be added to that used in increasing the kinetic energy of the molecules, to give the total heat absorbed. That is,

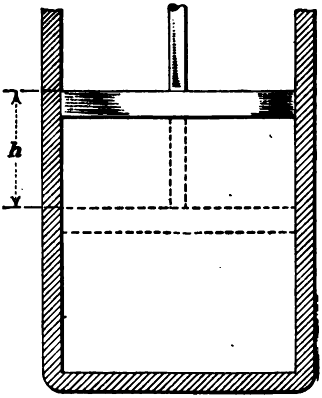

FIG. 8.

$$C_v(T_2 - T_1) + \text{work} = C_p(T_2 - T_1) = \tfrac{3}{2} R(T_2 - T_1) + R(T_2 - T_1)$$

or the molecular heat capacity at constant pressure is

$$C_p = \tfrac{5}{2} R = 4.97 \text{ cal., or } C_p - C_v = R. \qquad (12)$$

As mentioned above, this equation is applicable only in case energy is not used in increasing the rotation of the molecules, in causing their vibrations to increase, or in any other way than in increasing the kinetic energy of the molecules. At the time this equation was first developed the only monatomic gas known was mercury vapor, and it was considered a triumph of the kinetic theory that the molal heat capacity of this substance was equal to that required by equation (12). Since that time five other monatomic gases, the so-called rare gases of the atmosphere, have been discovered and subjected to experiment. As shown by the following table, these substances have the heat capacity to be expected from the kinetic theory of gases. It is indeed a useful equation from which we can predict the heat capacity of a substance before it has been discovered.

TABLE 16.—MOLAL HEAT CAPACITIES OF MONATOMIC GASES

Substance	C_p	$C_p - R = C_v$	Experiments by
Mercury vapor	4.97	2.98	Kundt and Warburg
Helium	5.10	3.11	Behn and Geiger
Argon	4.99	3.00	Niemeyer
Argon	4.97	2.98	Pier
Argon	5.07	3.07	Heuse[1]

Ratio of the Specific Heats at Constant Pressure and at Constant Volume.—In addition to the evidence derived from experiments on the temperature change during expansion into a vacuum (to be discussed presently), there is another way in which the correctness of equations (11) and (12) may be tested. It will be remembered that these equations were derived on the assumption that all of the energy added to the gas increased the kinetic energy of the molecules, or performed work in overcoming the pressure of the atmosphere during expansion. Let us assume for the moment that there is some unknown absorption of energy in addition to those stated. The equation $C_p - C_v = R$ has been established by experiment; and the quantity of energy $\frac{3}{2} R$ must be absorbed to increase the kinetic energy of the molecules and account for the experimentally proven increase in pressure with the temperature. Let x denote the energy required for the unknown uses mentioned above. Then the ratio of specific heats at constant pressure and at constant volume is

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[1] *Annalen der Physik*, **59**, 86 (1919).

$$\frac{C_p}{C_v} = \frac{5/2R + x}{3/2R + x} = \frac{5\,R + 2x}{3\,R + 2x}$$

It is possible to determine the ratio of these two specific heats from the velocity of sound in a gas,[1] and the ratio for monatomic gases is 1.667. Now this is 5/3, and hence x in the above equation must be 0. This shows that the equations derived above are supported by the results of experiment.

Heat Capacity of Diatomic Gases.—In case the molecules of a gas contain more than 1 atom, considerable quantities of energy may be absorbed in producing rotation of the molecule, or in producing internal vibrations (*i.e.*, displacement of one of the atoms relative to another). Experiment shows that the pressure of the diatomic and triatomic gases increases with the absolute temperature in the same way as that of the monatomic gases; which could be true only if the kinetic energy of the molecules increased with the temperature in the same way. The energy absorbed and converted into vibrations or rotations must therefore be in addition to that required to increase the kinetic energy of the molecules, and in addition to that required to do work against the atmosphere during expansion. Let us denote this additional energy by the term "internal energy," meaning thereby all of the energy absorbed which is not used in increasing the kinetic energy of the molecules or in external work. Then

$$C_p = 3/2R + R + E_{\text{int}}$$

and

$$C_v = 3/2R + E_{\text{int}},$$

It will be seen from these equations that the ratio C_p/C_v will be smaller than 5/3 in case E_{int} has a considerable value. Table 17 shows that this ratio is much smaller than 1.667; it is about 1.4 for diatomic gases, and it approaches unity as a limit as the internal energy increases in comparison to the increase of

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[1] The equation for this ratio is

$$\textit{sound velocity} = n\lambda = \sqrt{(p/d)\gamma} \qquad (13)$$

where n is the frequency or "pitch" of the sound, λ is its wave length, p and d are respectively the pressure and density of the gas, and γ is the ratio C_p/C_v for the gas in which the sound travels. It was derived by Laplace.

kinetic energy. Thus for ether, a gas molecule containing 15 atoms, the ratio[1] is only 1.08.

TABLE 17.—RATIO OF THE MOLAL HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE TO THOSE AT CONSTANT VOLUME[2]

Gas	Centigrade temperature	C_p	C_v	C_p/C_v
A	15	5.07	3.07	1.65
	−180	5.31	3.01	1.76
CO_2	20	8.88	6.85	1.30
	−75	8.07	5.90	1.37
N_2O	20	9.24	7.20	1.28
	−30	8.79	6.71	1.31
	−70	8.37	6.23	1.34
NO	15	7.25	5.25	1.38
	−45	7.17	5.16	1.39
	−55	7.26	5.25	1.38
	−80	7.33	5.31	1.38
CH_4	15	8.50	6.50	1.31
	5	8.42	6.41	1.31
	−30	8.14	6.12	1.33
	−55	8.08	6.05	1.34
	−80	8.08	6.03	1.34
C_2H_2	18	10.43	8.38	1.25
	−70	9.13	6.96	1.31
C_2H_4	18	10.22	8.18	1.25
	−36	9.17	7.08	1.30
	−68	8.79	6.63	1.33
	−91	8.64	6.41	1.35
C_2H_6	15	12.40	10.33	1.20
	−35	11.04	8.90	1.24
	−82	10.44	8.15	1.28

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[1] From the law of the equipartition of energy it can be shown that the heat capacity of a gas is $\frac{1}{2}R$ for each "degree of freedom" of its molecules. A diatomic molecule has 3 degrees of directional freedom (motion along the three axes) and 2 degrees of rotational freedom, about the two perpendicular axes which are each perpendicular to the line joining the centers of the atoms of the molecule. Thus the heat capacity of oxygen at constant volume should be $\frac{5}{2}R$ and at constant pressure $\frac{7}{2}R$, whence the ratio would be 1.40. These figures are in good agreement with the measured values recorded in the table. That the matter is not as simple as this is shown by an increase of the molecular heat capacity with the temperature. For this variation the kinetic theory has no simple explanation.

[2] Heuse, *Ann. Physik.*, **59**, 86 (1919).

TABLE 18.—RATIO OF THE HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE AND CONSTANT VOLUME

Gas	C_p/C_v
All monatomic gases[5]	1.667
Nitrogen[1]	1.414
Hydrogen[2]	1.403
Oxygen[5]	1.399
Carbon dioxide[3]	1.303
Carbon monoxide[5]	1.398
Water vapor[4]	1.37
Ammonia[5]	1.317
Benzol vapor[4]	1.13
Ether vapor[4]	1.08
Air[3]	1.403

Mass of Gas Striking a Unit of Surface.—Langmuir[6] has derived an equation expressing the mass of gas striking a square centimeter of surface per second. Since for a given temperature the average kinetic energy of the molecules is fixed, and the pressure is due to the impacts of gas molecules, it will be seen that this mass must be proportional to the pressure of the gas. The equation is

$$m = p\sqrt{\frac{M}{2\pi RT}} \tag{14}$$

where m is the mass of gas in grams striking a unit of surface, p is the pressure of the gas in dynes per square centimeter, M is the molecular weight of the gas, π is 3.1416, T is the absolute temperature and R has the value 8.32×10^7 ergs.

Energy Absorbed During Expansion when No Work is Done.—In the above derivation of the specific heat equation for monatomic gases at constant pressure (equation 12) it was assumed that all of the energy added was changed into the kinetic energy of the molecules or used in overcoming the external pressure.

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[1] Schulze and Rathjen, *Ann. Physik*, **49**, 457 (1916).

[2] Shields, *Phys. Rev.*, **10**, 525 (1917).

[3] Partington, *Physik Z.*, **14**, 969 (1914).

[4] Leduc, *J. Physique*, **6**, 5 (1916).

[5] Dushman, *Gen. Elec. Review*, **18**, 955 (1915).

[6] *Phys. Rev.*, **2**, 329 (1914).

There is another way in which energy might be used, and unless the quantity so used is zero, in a given case, equation (12) is not applicable to this case. If the molecules exert considerable attractive forces on one another, these forces will resist the expansion, and they must be overcome during expansion. If an experiment could be arranged in which no work was done during expansion, it would be possible to measure the energy required for the separation of the molecules against their own attractive forces, should these exist. Suppose one of the bulbs in Fig. 9 to be filled with a gas and the other to be evacuated; both being in a vessel of water containing a sensitive thermometer. When the stop cock is opened, gas will rush into the empty bulb and the pressure in the first vessel will fall until the pressure is the same in both bulbs. The gas does no external work in expanding into the vacuum, but the molecules of the gas are separated from each other. If work has been done in this separation, it must have been at the expense of energy absorbed from the gas itself or from the water in the calorimeter vessel, either of which would be shown by a change in the reading on the thermometer.

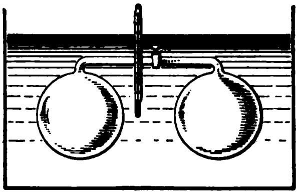

Fig. 9.

Experiments have shown that under the conditions here outlined, there was no appreciable fall in the temperature as shown by the thermometer, when the pressure of a gas was small. Under high pressures, however, the molecules of gases come close together, and do exert some attraction on each other. If such an expansion be carried out from high pressures, there will be a considerable decrease in temperature (called the Joule-Thomson effect) during the expansion; and if very sensitive measuring instruments be employed, small cooling effects will be observed with ordinary gases at moderate pressures. For monatomic gases the cooling effect has been found to be negligible, and equation (12) leads to values for the heat capacity of these gases which are in strict agreement with experiment. The cooling of diatomic and more complex gases is considered in the next paragraph.

Deviations from the Simple Gas Laws.—The simple law $pv = nRT$ no longer applies when the pressure is increased to quite high values, or when the gas approaches the temperature at which it condenses to a liquid under the applied pressure. The compressibility is less than that called for by this simple law; that is, doubling the pressure does not decrease the volume to half its original value. It is natural to conclude that compression does not change the volume of the molecules, but only decreases the free space between them. At high pressures, the volume occupied by the molecules becomes considerable in comparison with the total volume of the system. A better representation of the observed compressibility is obtained by modifying the equation to allow for the volume of the molecules, by writing it

$$p(v - b) = RT \tag{14}$$

where b is understood to be about the volume occupied by the substance of the molecules. It is perhaps the volume which the molecules would occupy if brought to rest; certainly it is not smaller than this, and it may be larger. Let us consider it as that part of the volume which is not compressed by increasing the pressure on the gas. By subtracting the incompressible volume b from the observed total volume v we bring our equation into better accord with the facts.

Joule-Thomson Effect.—In connection with the specific heat equation (page 49) the Joule-Thomson effect was mentioned. This effect is a cooling which is observed when a gas is allowed to expand from one pressure to a lower one without performing any external work, such as pushing back the atmosphere to make room for itself. If there were no attraction between the molecules, there should be no absorption of energy in overcoming it, and hence no decrease in the temperature of the gas. In the following table are shown some figures which illustrate the Joule-Thomson effect[1] for a pressure decrease of about 3 atmospheres.

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[1] Buckingham, *Bull. Bur. Standards*, **3**, 237 (1907).

TABLE 19.—COOLING OF GASES ON EXPANSION

Gas	Initial temperature	Observed cooling
Carbon dioxide	0°	4.82°
	40°	3.47°
	80°	2.90°
Oxygen	10°	1.07°
	90°	0.80°
Air	7°	0.88°
	90°	0.51°
Nitrogen	8°	1.03°
	90°	0.63°
Hydrogen	7°	−0.10°
	90°	−0.148°
	−80°	0.00°

Effect of Molecular Attraction—van der Waals' Equation. It may be seen from this table that the molecules do attract each other and that the cooling (which may be assumed a measure of the attraction) is different for different substances. This attraction tends to bring the molecules closer together, just as does the applied pressure; it should therefore be added to the pressure term to show that both the applied pressure and this "internal pressure," A, are compressing the gas. Our equation now stands, for a mol of gas,

$$(p + A)(v - b) = RT$$

A further inspection of the table will show that the attractive pressure, or internal pressure, decreases as the temperature is raised, therefore as the volume is increased by this rise of temperature. It is thus evident that the attractive pressure is a function of the molal volume itself. This is supported by the known fact that the deviations of actual gases from the simple law $pv = RT$ become smaller as the pressure becomes smaller, whereas if A is a constant, its importance would become greater relative to p at lower pressures. If we consider the layer of molecules about to strike a given wall at any instant of time, we see that the attraction holding them back will be proportional to the number of molecules back of them, *i.e.*, to the number of molecules attracting them. Since the number about to strike at any instant is also proportional to the number present, it follows that this attractive force is proportional to the square of the density of the gas, or inversely proportional to the square of the volume occupied by a mol of gas. Our equation may then be written with a/v^2 in place of A, when we have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{15}$$

This is the equation of van der Waals for the behavior of a mol of gas, though the argument on which it is based is not the same as that used in its original derivation. In this form the equation is able to represent quite accurately the behavior of gases under much higher pressures than those to which the equation $pv = RT$ is applicable; but it is of course much more difficult to handle. Unlike the simple gas law equation, it contains constants which depend on the nature of the gas under consideration The quantities a and b are different for different gases, and must be calculated from experiments on the particular gas under consideration; these values are shown in Table 20.

The equation of van der Waals also applies to the liquid state of substances; that is, it describes the compressibility of a liquid and its change of volume with changing temperature, though in a less satisfactory way than with gases. Near the critical region (the highest temperature at which condensation to a liquid is possible) the equation fails completely. It will be recalled that in the derivation we did not assume that the attraction between the molecules varied as any particular function of the distance between the molecules; we assumed only that the attractive force was dependent on the number of molecules. A proper knowledge of the change of forces acting between molecules with the distance between them will doubtless explain some of these deviations.

When the pressure becomes small and the volume of a mol of gas correspondingly large, the term a/v^2 becomes so small in comparison with p that it may be neglected; also the volume b

is negligible in comparison with the molal volume v, and it may be neglected. The equation of van der Waals thus reduces to the simple gas law at large molal volumes.

Richards[1] states that the quantity b is about 1.2 times the molal volume of the liquid substance at its boiling point, and that it represents essentially the volume of the molecules themselves. Others incline to the view that b is somewhat larger than the volume of the molecules, perhaps four times as large. The point has not yet been settled definitely.

TABLE 20.—VALUES OF VAN DER WAALS' CONSTANTS a AND b WHEN THE PRESSURE IS IN ATMOSPHERES, AND THE MOLAL VOLUME IN CUBIC CENTIMETERS[2]

Substance	b cubic centimeters per mol	a	Value of the attractive force a/v^2 at a molal volume of one liter
H_2	0.23	0.19×10^6	0.19 atm.
O_2	31.6	1.36×10^6	1.36
N_2	37.3	1.31×10^6	1.31
CO_2	42.8	3.61×10^6	3.61
CO	38.6	1.43×10^6	1.43
SO_2	56.5	6.69×10^6	6.69
C_2H_6	69.9	6.0×10^6	6.0
C_6H_6	120.3	18.71×10^6	18.7
CCl_4	127.3	20.86×10^6	20.9
H_2O	33.2	5.87×10^6	5.87
Ether	134.7	17.44×10^6	17.4
NH_3	36.4	4.05×10^6	4.0

Other Equations for Gases.—The equation of van der Waals is not by any means the only equation which has been proposed to represent the changes of pressure and temperature of a gas with volume; many others have been suggested from time to time, and new ones are constantly being proposed. In general it may be said that the accuracy with which a given equation expresses the behavior of an actual substances increases somewhat as the complexity of the equation employed increases, though this is not necessarily true. For a compressed gas is a highly complex system in which must be considered the attraction and repulsion of molecules for one another, the variation of these forces with the temperature, the variation of the volume of the molecules themselves with temperature, etc. It is not

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[1] *J. Amer. Chem. Soc.*, **36**, 629 (1914).

[2] For other data see *Z. physik. Chem.*, **69**, 52 (1910).

Table 21.—Pressure of Carbon Dioxide at Various Volumes.[1] Showing Deviations of Pressures Calculated from the Ideal Gas law, from van der Waals' Equation and from Keyes' Equation, from Experimental Pressures

Abs. temp.	Volume of a mol	Measured pressure, atmospheres	Calculated pressures and percentage deviations					
			Ideal gas law	Per cent	van der Waals	Per cent	Keyes	Per cent
273	1,320	15.07	17.0	13	15.4	2	15.10	0.2
	1,100	17.70	20.4	15	18.2	3	17.69	0.0
	880	21.22	25.5	22	22.1	4	21.33	0.5
	660	26.67	34.0	27	28.0	5	26.72	0.2
304	1,320	17.22	18.9	10	17.4	1	17.23	0.1
	1,100	20.32	22.7	12	20.6	2	20.30	0.1
	880	24.58	28.4	15	25.2	3	24.68	0.5
	660	31.36	37.9	20	32.1	2	31.41	0.2
321	1,320	18.40	19.9	8	18.5	1	18.40	0.0
	1,100	21.75	24.0	10	21.9	1	21.72	0.1
	880	26.41	30.0	14	26.8	2	26.52	0.5
	660	33.92	40.0	18	34.3	1	33.97	0.2
337	1,320	19.50	20.9	7	19.5	0	19.48	0.0
	1,100	23.08	25.1	9	23.1	0	23.05	0.1
	880	28.13	31.4	11	28.3	1	28.23	0.5
	660	36.31	41.9	13	36.5	1	36.36	0.2
373	1,320	21.98	23.1	5	21.9	0	21.95	0.2
	1,100	26.11	27.8	7	25.9	1	26.07	0.2
	880	32.01	34.7	8	31.9	0	32.11	0.4
	660	41.74	46.3	11	41.3	1	41.78	0.1

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[1] Keyes, *Amer. Soc. Refrig. Eng.*, **1916**, Dec. 4.

surprising that a simple equation is unable to take all of these features into account.

One recent equation which accords quite accurately with observed experimental data is that of Keyes,[1] which may be written

$p + \frac{a}{v^2} (v - b) = rT$

$$\left(p + \frac{a}{(v - l)^2}\right)(v - \delta) = RT \qquad (16)$$

where a and l are constants and the logarithm of δ is a function of the volume. Calculations based on this equation are rather difficult to carry out, but the agreement between observed and calculated pressures is excellent.

In Table 21 are shown the pressures of carbon dioxide corresponding to temperatures and molal volumes there given, together with the pressure calculated from the ideal gas law $pv = RT$; from van der Waals' equation, using the values of a and b given in Table 20; and from Keyes' equation, together with the percentage deviation of each of these calculated pressures from the experimental one. It should be noted that pressures calculated from the ideal gas law are seriously in error, and that this error is smaller for lower pressures and for higher temperatures. The deviations of van der Waals' equation are less serious, but are also smaller when the observed pressures are small and the temperature is high.

Molecular Diameters.—The quantity b in van der Waals' equation represents about the volume of the molecules themselves. A rough idea of the volume of a single molecule can be obtained by dividing the volume b, in cubic centimeters per molecular weight, by Avogadro's number; from which by extracting the cube root we obtain a measure of the diameter of a molecule. Two other equations of the kinetic theory, which are too complex to be considered here, also give a measure of the molecular diameter; one from measurements of the index of refraction of the gas, the other from measurements of the length of path of a molecule between collisions at small pressure. The results of these three methods agree remarkably, as will be seen[2] from Table 22. Other methods of estimating the diameter of single molecules will be taken up in later chapters, where they will be seen to be in good agreement with the figures derived from the kinetic theory.

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[1] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

[2] Dushman, *Gen. Elec. Review*, **18**, 1,049 (1915).

The value of *b* for ethane is 70 c.c. per mol. On dividing this by 6×10^{23} we obtain 115×10^{-24} c.c. as the volume of a single molecule. The cube root of this figure is roughly 5×10^{-8} cm., which is the diameter of a single molecule. The figures of Table 22, and those obtained by quite different methods in Chapter III, are all of this order of magnitude.

TABLE 22.—MOLECULAR DIAMETER IN CENTIMETERS, AS CALCULATED FROM EQUATIONS OF THE KINETIC THEORY OF GASES

Gas	From the average free path of a molecule	From the value of *b* in van der Waals' equation	From the index of refraction of a gas
H_2	2.4×10^{-8}	2.34×10^{-8}	1.9×10^{-8}
He	1.9×10^{-8}	2.65×10^{-8}	1.17×10^{-8}
NH_3	2.97×10^{-8}	3.08×10^{-8}	....
H_2O	....	2.89×10^{-8}	2.28×10^{-8}
CO	3.19×10^{-8}	3.12×10^{-8}	2.52×10^{-8}
N_2	3.15×10^{-8}	3.15×10^{-8}	2.42×10^{-8}
O_2	2.97×10^{-8}	2.92×10^{-8}	2.32×10^{-8}
A	2.87×10^{-8}	2.94×10^{-8}	2.36×10^{-8}
CO_2	3.36×10^{-8}	3.23×10^{-8}	2.78×10^{-8}
Hg	....	3.02×10^{-8}	....

Questions

1. Calculate the volume of a mol of helium at 100° and a pressure of 65 cm. of mercury.

2. Calculate the temperature at which a liter of helium under a pressure of 1 atmosphere weighs a gram.

3. A liter of gas at 20° and 1 atmosphere pressure weighs 2.66 grams. Calculate the molecular weight of the gas.

4. At what pressure will ammonia gas have the same density as air at 1 atmosphere, if the temperature is the same for each?

5. What would be the volume of a balloon having at 20° a lifting power of a ton (910 kilos) if it is filled with hydrogen? Assume the molecular weight of air to be 29.

6. Water gas is practically a mixture of equal mols of carbon monoxide and hydrogen. Calculate the weight of a liter of it under standard conditions. Calculate its lifting power in a balloon, in kilos per cubic meter of gas.

7. When air is passed over hot coke and cooled to the original temperature, the volume increases 6 per cent. Assuming that no oxygen remains, calculate the mol fraction of CO_2 and of CO in the gaseous mixture. What will be the molal weight of the mixture? Air may be assumed 21 mol per cent oxygen and 79 mol per cent nitrogen.

8. At 250° and 1 atmosphere PCl_5 is 80 per cent dissociated into chlorine and PCl_3. Calculate the weight of a liter of the mixture under these conditions.

9. When steam is blown through carbon at a red heat 80 per cent of it is converted into CO and hydrogen ("water gas"). Calculate the weight of a cubic foot of this gas at the mouth of the producer, where the temperature is 500° and the pressure is 1 atmosphere. What is the partial pressure of each gas? A cubic foot is 28 liters.

10. The pressure in an incandescent light bulb is about one dyne per square centimeter. If the gas in it is air, what is the weight of it in a 200 c.c. bulb? Calculate the actual number of molecules in the bulb. Assume a temperature of 20°.

11. Calculate the velocity of the oxygen molecules in air at 15°. Calculate the velocity of the nitrogen molecules.

12. At what temperature is the velocity of the oxygen molecules a mile per second? At what temperature is the velocity of hydrogen molecules 1 mile per second? (A mile is 1610 meters.)

13. If 100 c.c. of nitrogen under a constant pressure will flow through a given orifice in 155 sec., what is the density of a gas of which 100 c.c. under the same pressure will flow through the same orifice in 175 sec.? (*b*) Assuming the gas to be a mixture of nitrogen and argon, calculate the mol fraction of argon in it. (*c*) Calculate the time of flow for a mixture in which the mol fraction of the nitrogen is 0.50.

14. Calculate the mass of carbon dioxide striking each square centimeter of its containing vessel when the pressure is 0.001 atmosphere and the temperature 25°.

15. A liter of helium at 0°C. and 1 atmosphere pressure weighs 0.1785 grams. Calculate a value of the gas constant R.

16. Calculate the pressure at which carbon dioxide has a molal volume of 1,100 c.c. at 0°, employing the ideal gas law. Calculate this pressure from van der Waals' equation, using the values of a and b given in Table 20. (*b*) The observed pressure under these conditions is 17.70 atmospheres. Calculate the percentage error in each of the calculated pressures.

17. Make the same calculations as in question 16 for a temperature of 200°. The observed pressure at this temperature is 26.1 atmospheres.

18. Calculate the heat required to raise 25 grams of helium through 100 degrees at constant volume; at constant pressure.

19. What is the partial pressure of NO_2 in a mixture containing 45 per cent of it by weight and 55 per cent of N_2O_4? What is the apparent molecular weight of the mixture?

CHAPTER III

PROPERTIES OF SUBSTANCES IN THE LIQUID STATE

All of the substances which we were considering in the previous chapter as "gases," more properly termed substances in the gaseous state, may be changed to liquids by suitably increasing the pressure and lowering the temperature. A sufficient reduction in temperature will cause a gaseous substance to liquefy regardless of the pressure unless this is kept exceedingly small; but in general an increase of pressure will not cause a substance to liquefy regardless of the temperature. There is a certain "critical temperature" characteristic of each substance, above which its gaseous phase may not be liquefied, no matter how great the pressure exerted upon it. Similarly, nearly all of the familiar liquid substances may be changed to the gaseous state at higher temperatures or under low pressures. The liquid phase therefore, like the gaseous phase, depends upon the temperature and pressure for its existence.

Liquids are characterised by a greater resistance to flow (greater viscosity), by a much larger cohesive pressure, by a greater density and smaller compressibility than the same substances possess in the gaseous state. All of these changes are due to the much smaller distances between molecules; indeed the molecules in a liquid are probably touching each other a considerable portion of the time. These molecules exhibit the same kind of thermal vibrations that were considered under the kinetic theory of gases, but the molecules have less freedom of motion. They have shorter paths between collisions, the motions are seriously damped by the attractive forces acting between the molecules, which are much more powerful in virtue of the smaller distances separating the molecules, but the *kinetic energy* of their motion is the same as that in the gaseous state at the same temperature.

Miscibility.—While gases are capable of mixing with one another in all proportions, and without influencing the properties of each gas (such as its partial pressure), this is not true of liquids in all cases. Some pairs of liquids, such as alcohol and water, chloroform and carbon tetrachloride, benzene and xylene, do mix in all proportions; other pairs, such as aniline and water or ether and water, mix only to a limited extent; still others, such as benzene and water, alcohol and mercury, do not dissolve in each other to an appreciable extent. In the gaseous state all of these substances mix in all proportions, but this is doubtless because of the great separation of the molecules and the consequent lack of strong forces acting between them. In the liquid state, where molecules are very close to each other, specific attractive forces act between them, and these forces seem to govern the extent to which one liquid will dissolve in another. No general rules for solubility of liquids are free from exceptions, but it is usually true that liquids of the same chemical type (two hydrocarbons, two liquid metals, or water and alcohols) are soluble in each other, while liquids of quite different natures exhibit slight attractions for each other. Thus when benzene dissolves in toluene, its surrounding molecules are like it, and the attractive forces between molecules are not much altered. But, due to the great difference between benzene and mercury, there is no attraction between these molecules, and no mercury molecules separate from their own phase and enter the benzene phase. Mercury is therefore insoluble in benzene.

Molecular Attraction.—In the simple gas law, it was assumed that there were no attractive forces acting between the molecules; and it was found that at high pressures this assumption was not correct. To allow for it, a term (a/v^2) was introduced into the gas equation (van der Waals' equation). A molecular weight of water at 20° occupies about 18 c.c., and consists of the same molecules which form the vapor. But without the attractive forces which cause the vapor to condense (that is, assuming that water vapor was a perfect gas) the pressure necessary to bring a mol of gas into a space of 18 c.c. is given by $p \times 18 = 82 \times 293$, whence the pressure is 1,340 atmospheres. The pressure exerted by water at 20° (its vapor pressure) is only about 0.02 of an atmosphere. It appears that the attractive pressure, or *internal pressure*, must therefore be very large. The cause of molecular attraction is not fully understood but is believed to be due to stray electric fields caused by the electrons within the atoms. Whatever its cause, its existence is certain, and new researches dealing with it are rapidly clearing up some of the disputed points.

Many equations have been put forward by various investigators for calculating the internal pressure of a liquid from a/v^2, from the latent heat of evaporation, and from other data. But the internal pressures so calculated are not in good agreement with one another in most cases. The following table shows the internal pressure[1] in atmospheres according to the calculations of various workers. It should be borne in mind that all of these calculations are based on certain assumptions, and that the actual internal pressure has not been measured directly. The deviations among the values for any one liquid will indicate the uncertainty of the assumptions made as to the way in which the attractive forces act; but all of the calculations agree in showing that there is an internal pressure, and that it is very great.

TABLE 23.—INTERNAL PRESSURE (IN ATMOSPHERES) OF VARIOUS LIQUIDS

	Winther[2]	Traube[3]	Walden[3]	Lewis[4]	Mathews[5]
Ether	1,220	990	1,360	1,930	1,970
Ethyl acetate	1,490	1,140	1,730	2,640	2,460
CCl_4	1,820	1,305	1,680	2,520	2,660
Benzene	1,790	1,380	1,920	2,640	2,940
Chloroform	1,680	1,410	1,950	2,780	2,910
CS_2	2,200	1,980	2,400	2,920	3,950
Ethyl alcohol	2,030	2,160	4,000	.....	3,600

Surface Tension.—When a wire ring is dipped into a liquid a continuous film of liquid may form within it, due to the attraction between molecules in the liquid. In the bulk of liquid this force is exerted equally in all directions, but molecules in a surface exert a force which has a resultant *in* the surface layer. This same force of attraction holds a drop of liquid suspended on a rod, and limits the size of a drop which may be so held; it causes the suspended drop to assume a spherical shape and thus reduce its surface to a minimum. Surface tension is measured in dynes per centimeter. If a ring has within it a continuous film of liquid, the surface tension causes a certain force to be directed toward the center of the ring for each centimeter of ring circumference. It is not correct to speak of surface tension per square centimeter, for such a force could not act within the surface, but outside it. The force here concerned is in dynes per centimeter length of surface film, it acts within the plane of the surface, and perpendicular to the direction in which the length of film-edge is measured.

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[1] Hildebrand, *J. Am. Chem. Soc.*, **38**, 1,459 (1916).

[2] From optical properties.

[3] From surface tension and van der Waals' *a* and *b*.

[4] From thermal data.

[5] From latent heats and surface tension.

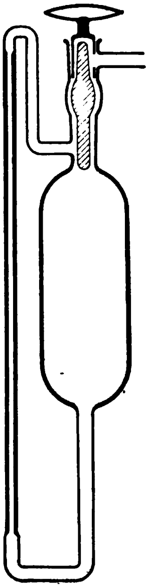

FIG. 10.—Apparatus for measuring capillary rise.

The rise of a liquid in a capillary tube which is wet by the liquid may be used as a measure of its surface tension. If γ is the tension in dynes per centimeter, and h is the height to which a liquid of density d rises above the horizontal surface in a tube of radius r, the equation connecting these quantities is

$$\gamma = \frac{rhdg}{2} \tag{1}$$

This equation results from equating the surface tension to the weight of liquid raised by it when equilibrium of forces is reached. The length of film edge is the circumference of the tube, $2\pi r$, hence the force is $2\pi r\gamma$, and this is balanced by a volume of liquid πr^2h of density d acted upon by the force of gravity, g. It follows from this that $2\pi r\gamma = \pi r^2hdg$, and upon solving for γ, equation (1) results.

Much of the data on surface tension measured from the rise in capillary tubes is in error[1] on account of failure to measure the height h above a *horizontal* surface. The tube in which the flat surface is measured should be at least 3 cm. in diameter in order to have a horizontal surface in it; smaller tubes exhibit a capillary rise of their own which renders a capillary rise relative to such a surface incorrect. Richards' apparatus is shown in

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[1] Richards, *J. Am. Chem. Soc.*, **37**, 1,656 (1915).

Fig. 10. The height of capillary rise is measured with a cathetometer by focusing on the horizontal surface in the large bulb, then on the capillary meniscus in the tube connected to the bulb. Some measurements by this method are shown in Table 24.

TABLE 24.—SURFACE TENSION OF PURE LIQUIDS
(Measured in dynes per centimeter at 20° by the capillary rise method)

Water	72.62	Toluene	28.58
Benzol	28.88	Isobutyl alcohol	22.85
Methyl alcohol	22.61	Ethyl butyrate	24.54
Ethyl alcohol	22.27		

Surface Tension and Drop Weight.—Under proper conditions the weight of a drop which causes it to detach itself from the end of a capillary tube and fall under the influence of gravity may be used to determine the surface tension of a liquid,[1] since the drop weight is directly proportional to the surface tension for a given tube tip. This relation between drop weight and surface tension is shown in Table 25.

TABLE 25.—COMPARISON OF SURFACE TENSION AND DROP WEIGHTS FOR A GIVEN CAPILLARY TIP

Substance	Temperature	Surface tension = γ	Milligrams per drop = W	$\frac{W}{\gamma}$
Ether	20°	16.80	21.4	1.27
Chlorbenzene	20°	32.10	41.4	1.30
Water	20°	70.60	89.1	1.26
Benzene	22.5°	29.38	35.2	1.21
Ethyl iodide	19.1°	30.00	36.1	1.20
Benzaldehyde	15.4°	39.19	49.8	1.27
Aniline	17.5°	44.10	52.9	1.21
Quinoline	15.4°	45.13	57.0	1.26

This furnishes a ready means of measuring the relative surface tensions of liquids in terms of that of any one liquid as a standard, or of measuring the surface tension at one temperature in terms of that of the same liquid at another temperature.

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[1] Morgan, *J. Am. Chem. Soc.*, **30**, 1,055 (1908); **33**, 657 (1911); **35**, 1,249, 1,505, 1,750 (1913); Harkins, *J. Am. Chem.* Soc., **39**, 572 (1917); compare Lohnstein, *Z. physik. Chem.*, **84**, 410 (1913) for a criticism of the method.

Surface Tension and Temperature.—The empirical equation of Ramsay and Shields shows the change of molecular surface energy with temperature, where the molecular surface energy is proportional to the product of surface tension and the molecular volume to the $\frac{2}{3}$ power. The equation is

$$\gamma(Mv)^{2/3} = k(t_c - t - d) = k(\tau - d) \tag{2}$$

where t_c is the critical temperature, t is the temperature at which γ is measured, and τ is the difference between the critical temperature and the temperature of experiment. The quantity $(Mv)^{2/3}$ is proportional to the surface exposed by a mol of liquid; it changes only slightly with the temperature. From the equation it is seen that the surface tension γ decreases as the critical temperature is approached, and that it becomes zero when $(t_c - t)$ is equal to d. The quantity d is a correction factor of 6°, made necessary through some unknown cause, and it is introduced into the equation to show that γ becomes zero at 6° below the critical temperature, in place of at the critical temperature as might be expected. The value of k in the equation is obtained from measurements of γ at different temperatures for one substance; it has the same value for all normal substances. As is also the case with other equations to be given in this chapter, this equation fails to hold for certain liquids which are in some way abnormal; these substances are said to be associated into double and more complex molecules in the liquid state. But for liquids which consist of single non-associated molecules, this equation describes the change of surface tension with temperature in a satisfactory manner. As liquid and vapor do not become identical until the critical temperature is reached, it is difficult to understand why the "correction" term of 6° appears in the Ramsay equation, but if critical temperatures are calculated from the temperature change of surface tension, or from drop weight which is proportional to it, without using this correction term, they are uniformly 6° too low. Critical temperatures calculated with the use of this factor are in surprising agreement with those obtained by direct measurement. In Table 26 are shown some calculations based on drop-weight measurements at two temperatures. The Ramsay equation written as a drop-weight equation is

$$w(Mv)^{2/3} = K(t_c - t - 6)$$

where w is the drop weight and the other terms have the same meaning as before. Critical temperatures for quinoline and pyridine have not yet been measured, but it will be seen that the value of K derived from measurements at different temperatures is the same as for the other substances, which is evidence that their calculated critical temperatures are as nearly correct as the others in this table.

TABLE 26.—CRITICAL TEMPERATURES CALCULATED FROM DROP WEIGHTS AT DIFFERENT TEMPERATURES[1]

Substance	Milligrams Weight per drop at		$w(Mv)^{2/3}$ at		K	t_c Calculated	t_c Experiment
	18°	60°	18°	60°			
Benzene	30.96	25.10	614.99	516.44	2.326	288	288
Quinoline	48.10	43.09	1,156.42	1,057.23	2.329	520	
CCl_4	28.85	23.55	607.14	512.89	2.332	285	283
C_6H_5Cl	35.87	30.48	780.31	682.00	2.328	360	359
Pyridine	40.37	34.14	751.71	654.35	2.330	347	

Vapor Pressure.—The pressure at which a liquid and its vapor are in equilibrium at a definite temperature is called the vapor pressure of the liquid. When not in contact with its liquid phase, a vapor may exist at any pressure lower than its vapor pressure. If the volume of such a vapor is gradually decreased at some temperature below its critical temperature, the pressure increases approximately in accordance with the simple gas law, until the vapor pressure is reached. Any further decrease in volume does not increase the pressure, but causes the formation of a liquid phase. As the volume is still further decreased, the pressure remains constant until all of the vapor has condensed to liquid; after which the pressure may be increased to any desired extent. There is only one pressure for a given temperature at which the liquid phase and the gaseous phase may exist in equilibrium, but either phase may exist alone over a considerable range of pressures for any given temperature. It should be clearly understood that a vapor pressure is an equilibrium pressure. The partial pressure of water vapor in the absence of liquid may be anything less than its vapor pressure and remain indefinitely so, but its vapor pressure is a saturation pressure at which vapor and liquid will remain indefinitely at equilibrium. The humidity of air, for example, is the ratio of the partial pressure of water vapor in it to the saturation pressure of water at the temperature in question. The pressure of water vapor and the vapor pressure of water are identical only when the humidity is unity.

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[1] Morgan and Thomssen, *J. Am. Chem. Soc.*, **33**, 657 (1911).

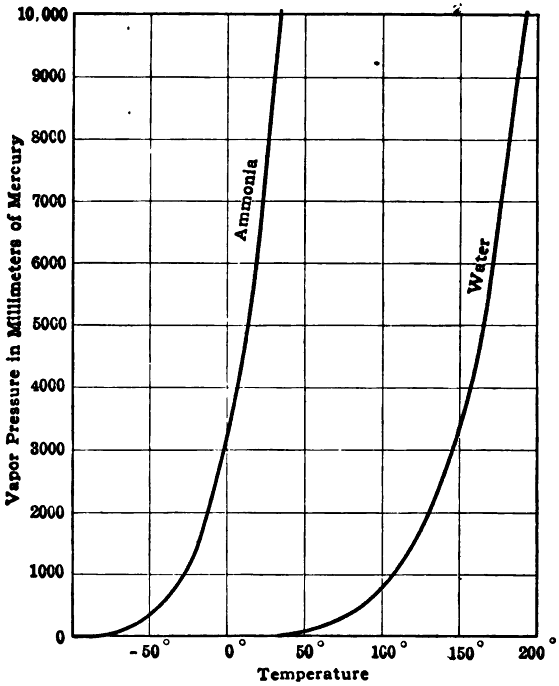

FIG. 11.—Change of vapor pressure with temperature.

Vapor Pressure and Temperature.—The vapor pressures o all liquids increase rapidly as the temperature is increased. Thi is seen in the data for water, Table 27, and for ammonia, Tabl 28, which are shown in Fig. 11.

TABLE 27.—VAPOR PRESSURE OF WATER,[1] IN MILLIMETERS OF MERCURY

Temperature	Vapor pressure	Temperature	Vapor pressure
−15	1.445	60	149.19
−10	2.160	70	233.53
−5	3.171	80	355.1
0	4.579	90	525.8
5	6.543	100	760.0
10	9.210	110	1,074.5
15	12.794	120	1,488.9
20	17.539	130	2,025.6
25	23.763	140	2,709.5
30	31.834	150	3,568.7
35	42.188	160	4,633.
40	55.341	170	5,937.
45	71.90	180	7,514.
50	92.54	190	9,404.
55	117.85	200	11,647.

TABLE 28.—VAPOR PRESSURE OF AMMONIA[2] IN MILLIMETERS OF MERCURY

Temperature	Vapor pressure	Temperature	Vapor pressure
−80°	37.6	0°	3,221
−70°	81.9	10°	4,612
−60°	164.2	20°	6,428
−50°	306.6	30°	8,749
−40°	538.3	40°	11,658
−30°	896.7	50°	15,245
−20°	1426.8	60°	19,606
−10°	2181.4	70°	24,842

The rate at which the vapor pressure of a liquid changes with the absolute temperature is shown by the following exact equation, called the Clausius-Clapeyron equation, and based on thermodynamics alone.

$$\frac{dp}{dT} = \frac{L}{(V_g - V_l)T} = \frac{L}{T\Delta V} \tag{3}$$

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[1] *Annalen der Physik*, **26**, 832 (1908); **29**, 723 (1909); **31**, 715, 945 (1910).

[2] Craghoe, Meyers and Taylor, *J. Am. Chem. Soc.*, **42**, 228 (1920).

In this equation L is the quantity of heat required to vaporise V_l cubic centimeters of liquid to form V_g cubic centimeters of vapor at the temperature T, and dp/dT is the rate at which the vapor pressure increases with the temperature. ΔV is therefore the increase in volume attending evaporation.

For approximate calculations involving evaporation at pressures not much greater than 1 atmosphere, this equation can be much simplified by neglecting the volume of liquid V_l in comparison with that of the vapor V_g (which is over a thousand times the liquid volume), and by expressing V_g with the aid of the ideal gas law $pV_g = RT$ for one mol of vapor formed. The equation then becomes

$$\frac{dp}{dT} = \frac{Lp}{RT^2} \tag{4}$$

where L is now the molal heat of evaporation, since 1 mol of vapor is formed, and R is the usual gas constant, expressed as 1.99 cal. when the molal latent heat of evaporation L is so expressed. Over small ranges of temperature the latent heat is practically constant, and with this assumption the equation may be integrated between limits in order to facilitate calculating the vapor pressure at one temperature from that at some other temperature. The integrated expression is[1]

$$2.303 \log \frac{p_2}{p_1} = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5}$$

As the pressures involved appear as a ratio, p_2/p_1, they may be expressed in any units desired; similarly L and R appear as a ratio and should be expressed in the same units, commonly calories.

An approximate equation for the vapor pressure of a substance in terms of its critical temperature and pressure is due to van der Waals. The equation is

$$\log \frac{p_c}{p} = c\left(\frac{T_c}{T} - 1\right)$$

where p_c and T_c are the critical pressure and temperature (page 78), and p is the vapor pressure at the temperature T. The constant c is usually taken as 3, but is smaller for monatomic gases and the halogens, and greater than 3 for some substances.[1]

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[1] In this book the abbreviation log signifies logarithms to the base 10, that is, ordinary logarithms; natural logarithms, to the base $e = 2.7183$, are abbreviated ln. Then $\ln x = 2.303 \log x$.

Boiling Point.—The boiling point of a liquid is the temperature at which its vapor pressure is 760 mm. of mercury, or 1 atmosphere. The temperature at which a liquid is observed to boil in the laboratory under atmospheric pressure is a variable quantity depending upon the location of the laboratory and the existing barometric pressure. It is often necessary to apply a correction to such observed boiling points in order to reduce them to standard boiling points. This correction is usually smaller than a degree, but in places of high altitude it may be very much larger; failure to make such corrections in reporting boiling points has led to small errors in recorded data. It is partly for this reason that the melting point of an organic substance (which is not affected by changes of pressure) is a better guide to its purity than the boiling point.

The rise in boiling point of a pure liquid per millimeter increase in external pressure is roughly the same fractional amount of the absolute-scale boiling point for all substances, about 0.0001. To compute a true boiling point from one observed at some pressure higher than 760 mm. multiply the excess pressure over 760 mm. by 0.0001 of the absolute boiling point, and subtract this product from the observed boiling point, *i.e.*, subtract $\Delta t = 0.0001T \times \Delta p$. For example, under 772 mm. pressure water boils at $373 \times 0.0001 \times 12 = 0.45°$ higher than at 1 atmosphere, according to the rule just given; the difference in boiling point for 12 mm. pressure found by experiment is 0.44°. When the barometric pressures are below atmospheric pressure, the corrections should of course be added to the observed boiling points. For pressures far removed from atmospheric, this simple rule will not give the proper correction. Thus at 525 mm. pressure the boiling point of water calculated according to this rule is 92.2°; the experimental boiling point under this pressure is 90.0°. When it is desired to calculate boiling points at pressures considerably removed from 1 atmosphere, the approximate form of the Clausius-Clapeyron equation (5) will give results of reasonable accuracy; thus in the case just considered, by substituting 9,700 cal. for L, 1.99 cal. for R, 760 and 373 for

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[1] Herz, *Z. Elektrochemie*, **25**, 408 (1919).

TABLE 29.—Boiling points, latent heats, and critical data[1]

Substance	Molal weight (1)	Absolute boiling point (2)	Absolute critical temperature (3)	Molal heat of vaporization (4)	Critical pressure, atmospheres (5)	Critical density (6)	Molal latent heat (Trouton) (7)	Molal latent heat (Hers) (8)	$\frac{d_{crit}}{d_{theor}}$ (9)	$\frac{T_{crit}}{T_{B.pt}}$ (10)
Helium	4.00	4.25	5.25	.....	2.26	0.060	86.3	100	2.8	1.23
Argon	39.9	87	156	.....	48.	0.509	1,765	2,520	3.4	1.79
Krypton	82.92	121	210	.....	54.3	......	2,450	......	....	1.73
Xenon	130.2	164	288	.....	57.	1.15	3,330	4,300	3.66	1.75
Hydrogen	2.0	20.5	38.5	.....	13.4	0.0257	416	620	3.39	1.88
Oxygen	32.00	90.1	155	1,600	49.30	0.430	1,830	2,460	3.46	1.70
Nitrogen	28.0	77.3	128	1,330	33.65	0.311	1,570	......	....	1.64
Chlorine	70.92	240	414	2,390	79.6	......	4,870	......	....	1.72
Nitric oxide	30.0	123	179.5	.....	71.2	......	2,500	......	....	1.45
HCl	36.5	190	324	3,600	81.5	0.41	3,860	4,820	3.68	1.70
HBr	80.93	204	363	3,940	84.4	......	4,160	......	....	1.79
CO	28.0	83	135.3	1,430	34.60	0.3110	1,680	2,070	3.56	1.63
CO_2	44.0	194.7	304	.....	72.85	0.448	3,950	4,750	3.49	1.57
N_2O	44.0	183.2	309.5	4,400	71.65	0.454	3,720	4,400	3.65	1.69
Methane	16.0	108.3	190.15	.....	54.6	0.1623	2,200	3,000	3.47	1.77
Ethane	30.1	190	305.1	.....	48.85	......	3,850	.....	....	1.60
Ethylene	28.0	168	282.5	.....	50.65	......	3,410	.....	....	1.68
Acetylene	26.0	...	308.5	.....	61.65	......	.....	.. ..	....	....
Cyanogen	52.1	252	401.3	5,360	59.75	......	5,120	.....	....	1.58
Sulfur dioxide	64.0	263	430.1	6,150	77.65	0.513	5,350	6,400	3.64	1.63
Ammonia	17.0	239	406	5,500	112.3	0.2362	4,850	5,380	4.21	1.69
Water	18.0	373	647	9,700	217.5	0.40	7,570	6,500	4.97	1.72
Hydrogen sulfide	34.0	213	373.4	4,500	89.05	......	4,340	.....	....	1.75
CCl_4	153.8	350	556	7,200	45.	0.56	7,100	7,800	3.68	1.59
$SnCl_4$	260.5	387	592	7,950	37.	0.742	7,860	8,660	3.73	1.53
Methyl alcohol	32.1	338	519	8,420	78.6	0.272	6,870	6,260	4.58	1.53

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Ethyl alcohol	46.1	351	516	9,960	63.	0.276	7,130	7,000	4.00	1.47
Propyl alcohol	60.1	370	537	.....	50.	0.273	7,500	7,300	4.00	1.45
Ether	74.1	307.6	467.5	6,260	35.6	0.263	6,140	6,620	3.82	1.52
Formic acid	46.0	374	......	5,550	......	......	7,600	.....	....	....
Acetic acid	60.	391	594	5,650	57.2	0.351	7,830	6,540	4.99	1.52
Methyl formate	60.	305	487	6,840	59.5	0.350	6,200	6,720	3.92	1.60
Methyl acetate	74.1	334	507	7,300	46.5	0.327	6,800	6,900	3.94	1.52
Methyl propionate	88.1	356	530	7,660	39.5	0.313	7,240	7,420	3.91	1.49
Methyl butyrate	102.1	375	554	7,900	34.3	0.300	7,620	7,800	3.90	1.48
Methyl *iso* butyrate	102.1	365	541	7,770	34.	0.301	7,320	7,700	3.87	1.48
Ethyl formate	74.1	331	508	7,340	46.7	0.324	6,730	6,910	3.89	1.54
Ethyl acetate	88.1	350	523	7,600	38.	0.308	7,110	7,260	3.95	1.50
Ethyl butyrate	116.1	394	566	8,550	30.2	0.276	8,000	8,850	3.65	1.43
n-Pentane	72.1	309	470	6,070	33.	0.230	6,280	6,780	3.76	1.52
n-Hexane	86.1	343	508	6,820	29.6	0.234	7,000	7,320	3.83	1.48
n-Heptane	100.2	371	540	7,400	27.2	0.234	7,550	7,900	3.85	1.46
n-Octane	114.2	399	569	8,150	24.6	0.233	8,100	8,500	3.86	1.42
iso Pentane	72.1	303	461	5,900	33.	0.234	6,150	6,900	3.73	1.52
Benzene	78.1	353	561	7,450	48.	0.305	7,180	7,700	3.76	1.59
Fluorbenzene	96.1	358	560	7,620	44.6	0.354	7,280	8,100	3.80	1.56
Chlorbenzene	112.5	405	632	8,440	44.6	0.366	8,230	8,800	3.78	1.56
Brombenzene	157.	429	670	8,750	44.6	0.485	8,700	9,250	3.81	1.56
Iodobenzene	204.	461	721	9,440	44.6	0.581	9,350	10,400	3.78	1.56

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[1] Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910); Van Laar, *Chem. Weekblad.*, **16**, 1,557 (1919); Cardoso, *J. chimie physique*, **10**, 470 (1912); **13**, 312 (1915); Walden, *Z. physik. Chem.*, **65**, 257 (1909).

T_2 and p_2, 525 for p_1, and solving for T_1, we find $T_1 = 364.0$, whence t is 91°. This will illustrate the divergence to be expected from the use of these two approximate rules. The error in the latter calculation is not due to any fault in the Clausius-Clapeyron equation, which is absolutely exact, but is a result of simplifying it by means of assumptions which are only approximately correct.

Critical Conditions.—As was mentioned at the beginning of the chapter, there is for each substance a **critical temperature** above which it cannot exist as a liquid. At any temperature below this critical one a substance becomes liquid when the applied pressure is greater than the vapor pressure of the substance at that temperature. But at temperatures higher than the critical the liquid phase does not appear, no matter how great the pressure. The **critical pressure** is the pressure which causes the liquid phase to form at the critical temperature. It is thus the last point on the vapor pressure curve. The **critical density** is the density of the liquid and of the vapor at the critical temperature and pressure. Under these conditions the liquid phase and the vapor phase are identical in all properties. The **critical volume** is the volume of a gram of substance under the critical temperature and pressure.

Numerical data relating to the critical properties of substances, together with other data to be used in this chapter, will be found in Table 29.

Many equations of an empirical nature have been proposed to show the relation between critical constants and other properties of substances, but they are not applicable to all substances, and there seems to be no simple rule for determining whether a chosen equation will describe the behavior of a substance or not. Nearly all writers consider a substance as "normal" in its behavior when it conforms to some particular equation, but substances which are normal according to one equation are often abnormal when judged by some other equation. Some of these equations are here given; when actual data are lacking they are useful in estimating a rough value of critical constants.

It has been known for some time (law of Guldberg-Guye) that the critical temperature of a substance was about three-halves its boiling point, each on the absolute scale. That is

$T_c/T_b = 1.5$ for many substances. The values of this ratio are given in column 10 of Table 29, where the maximum variations are seen to be 1.42 to 1.88, except in the case of helium. The validity of the Guldberg-Guye law is doubtful in some cases.[1]

Young[2] states that the critical density is about 3.7 times the theoretical density of the vapor as calculated from the ideal gas law $pv = RT$. Some substances deviate from this rule quite widely; water, acetic acid, methyl alcohol and ammonia are examples, see column 9 of Table 29. These substances also do not conform to the simple rules relating to heat of evaporation, and are for other reasons considered to be abnormal. Their abnormality probably consists in a more or less close chemical combination of the molecules into double and larger aggregates; at least such a combination offers a ready explanation of the deviations. These will be considered more fully at the end of the chapter, but they should be kept in mind while the various rules are under discussion.

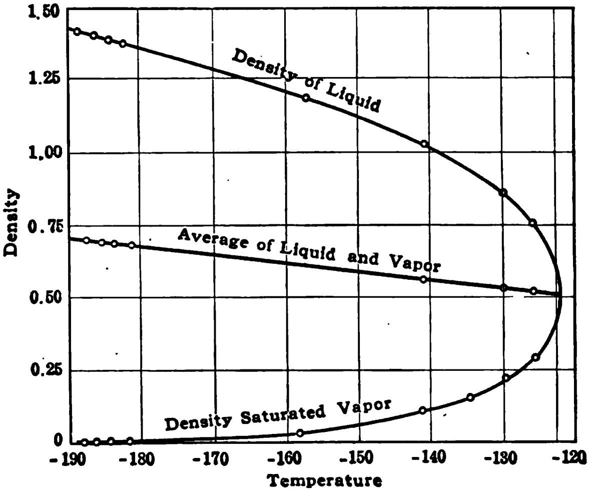

FIG. 12.

Law of Average Densities.—As the temperature is raised, the density of saturated vapor increases rapidly, owing to the increase of vapor pressure of the liquid. The density of the liquid phase decreases as the temperature is raised; at first slowly then more rapidly as the critical temperature is approached. At the critical temperature the density of liquid becomes the same as that of the saturated vapor; there is therefore in this region considerable difficulty in distinguishing the separate phases, and an exact determination of the critical density is difficult. It has been found that as the critical temperature is approached, the average of the density of the liquid and its saturated vapor is a linear function of the temperature. This statement will be clearer from an examination of Figures 12 and 13. By plotting this average density against the temperature and drawing a straight line through the points it is easy to determine the point at which this line intersects the curve showing the density of each phase, and thus to read the critical density. This statement is also known as the law of Cailletet and Mathias,[1] after its discoverers, and as the law of rectilinear diameters, since the diameter of the density curve is a straight line.

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[1] Moles, *J. chimie physique*, **17**, 415 (1919).

[2] *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

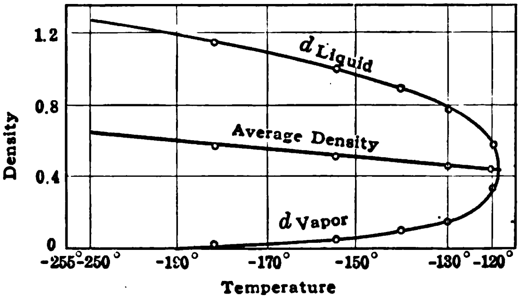

Fig. 13.

Latent Heat of Evaporation.—Energy is required to overcome the attractive forces acting between the molecules of a liquid; and hence in separating them during evaporation a considerable quantity of heat is required. This heat added to a boiling liquid does not raise the temperature of it or of its vapor, but it is used in the expansion which takes place when a liquid changes to a vapor. If the evaporation takes place into a vacuum, all of the heat is used in separating the molecules of the substance. When the evaporation takes place in the atmosphere, as is usually the case, a certain volume of the air must be pushed back to allow space for the vapor formed. This work is also done at the expense of heat added during the evaporation. Hence evaporation at atmospheric pressure requires more heat than evaporation into a vacuum. The volume of a mol of vapor is RT (that is, 82 T) cubic centimeters when the pressure is 1 atmosphere, and this volume of air must be displaced by the vapor formed. Suppose the liquid to be vaporized in a vessel fitted with a piston; as vapor forms, the piston rises to make room for it, thus lifting up the column of air above it. The work done is the product of force times distance, or pressure times the area of the piston times the height through which it rises. But the product of area times height is the volume of the vapor formed, hence pv is the work done. This is RT cubic-centimeter-atmospheres, or RT calories per molecular weight of vapor formed, and the molecular heats of vaporization into a vacuum and against the atmosphere therefore differ by this amount. If the difference is desired in calories, R has the value 1.99; in cubic-centimeter-atmosphere units R is 82. One calorie is thus equivalent to 41.24 c.c.-atm.

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[1] *Compt. rendus*, **102**, 1,202 (1886).

The quantity of heat required per molecular weight of vapor formed from its liquid is called the molecular heat of vaporization, or the molal latent heat. Its value is roughly the same for all liquids of the same boiling point; it is larger for liquids of high boiling point and smaller for those of low boiling point. This fact is expressed in the so-called **Trouton's rule,** which states that the molal latent heat of evaporation in calories is about 20.3 times the boiling point, on the absolute scale, when the evaporation takes place under 1 atmosphere pressure. This is expressed by the equation

$$\frac{L}{T} = 20.3 \qquad (7)$$

When evaporation takes place at a higher pressure than 1 atmosphere, and hence at a higher temperature, smaller latent heats are observed. This decrease continues until at the critical point no heat is required to evaporate the liquid.

Trouton's rule, like many empirical laws, is an approximation of considerable usefulness when rough data are desired; but it is not strictly exact. The deviations are shown in Table 29, in which the figures of column 7 should be the same as those of column 4 if there were no deviations of the rule. In homologous series of compounds the value of the Trouton constant increases somewhat as the boiling point of the liquid increases.

Many modifications of Trouton's rule have been suggested from time to time; most of which bring some classes of substances into better agreement than is obtained with the simple Trouton rule. Nernst proposes

$$\frac{L}{T_b} = 9.5 \log T_b - 0.007T_b. \tag{8}$$

Forcrand[1] gives a more complicated function,

$$\frac{L}{T_b} = 10.1 \log T_b - 1.5 - 0.009T_b + 0.0000026T_b^2 \tag{9}$$

Hildebrand[2] suggests that a better value of L/T is obtained when the evaporation takes place at such a temperature that equal concentrations of vapor are obtained.

In estimating molal latent heats where no data exist, the simple Trouton rule will probably be found as satisfactory as any of its modifications, since the latter are not reliable in every case, and there is no simple rule for determining whether the liquid in question is a "normal" substance or not.

Herz[3] gives a relation between the latent heat of evaporation and the critical temperature, critical pressure and critical density, based on the fact that the product Mp_c/T_cd_c has the same value as the Trouton constant, L/T_b, where M is the molecular weight, T_b the boiling point, and the other terms refer to the critical data. By substituting for T_c its approximate equivalent $1.5T_b$ (Guldberg-Guye law) and equating the two terms given above, the equation

$$L = \frac{2Mp_c}{3d_c} \tag{12}$$

is obtained. The latent heats so calculated are shown in Table 29, column 8. They should be compared with those derived from Trouton's rule, and with those derived from direct experiment.

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[1] *Compt. rendus*, **156**, 1,439 (1913).

[2] *J. Am. Chem. Soc.*, **37**, 970 (1915).

[3] *Z. Elektrochem.*, **25**, 321 (1919).

Viscosity.—By the viscosity, or internal friction, of a liquid is meant its resistance to flow, which is a measure of the friction between the liquid layers as they slide over one another through a pipe or tube. The absolute unit of viscosity is the force in dynes which is necessary to move a square centimeter of liquid surface with unit velocity past a stationary liquid surface 1 centimeter away from it. Measurements are made by flowing the liquid through a small tube of known dimensions under a measured pressure, or from the oscillations of a disc suspended in the liquid. It is necessary in making such measurements that the flow of liquid be parallel to the sides of the tube, and not turbulent in character, since the resistance to turbulent flow is greater than the resistance to "stream line" flow. This means only that the tube must be quite small for liquids of low viscosity.

The viscosity of a liquid relative to that of water at the same temperature is more commonly measured, and is called "relative viscosity."

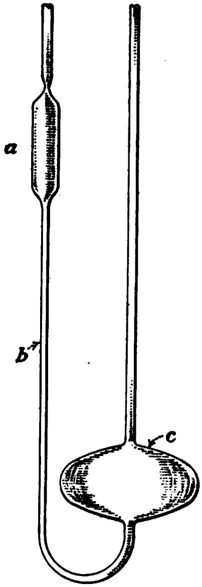

FIG. 14.—Washburn type of viscosimeter.

One type of instrument[1] for measuring relative viscosity is shown in Fig. 14. It consists of a bulb *a* for measuring the quantity of liquid flowing, a capillary tube *b* and a receiving vessel *c*. By applying pressure to the tube above *c*, the liquid is forced into the upper bulb until it stands somewhat above the upper mark, the pressure is then released, and time is measured while the meniscus passes from the mark above the bulb *a* to the mark below this bulb. As the driving force is a column of the liquid itself, this force varies with the density of the liquid, and it is necessary to multiply the time of flow by the density in making a comparison. Thus denoting by η the viscosity, D the density and t the time of flow of an unknown liquid through a given viscosimeter, and by η_w, D_w and t_w the corresponding quantities for water, the relative viscosity of the unknown liquid

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[1] Washburn and Williams, *J. Am. Chem. Soc.*, **35**, 737 (1913).

(referred to that of water as unity) is given by the expression

$$\frac{\eta}{\eta_w = 1} = \frac{Dt}{D_w t_w}. \qquad (13)$$

Relative viscosities obtained in this way may be changed to those in terms of the absolute system by multiplying the numbers so obtained by the viscosity of water at the temperature in question. These values are as follows:

TABLE 30.—VISCOSITY OF WATER[1]

t	η	η_t/η_0
0	0.01793	1.0000
10	0.01310	0.7300
18	0.01057	0.5898
25	0.00893	0.4974
40	0.00657	0.3668
50	0.00550	0.3064
75	0.00380	0.2120
100	0.00284	0.1584

Liquids increase their viscosity considerably when under pressure, especially at low temperatures, and the increase for a given unit of pressure is greater at higher pressures. All liquids decrease in viscosity at higher temperatures, the decrease for water near room temperature being about 2 per cent for each degree rise in temperature. (It should be noted that gases *increase* in viscosity at higher temperatures, as on account of the increased number of collisions the molecules interfere with each other to a greater extent.)

Arrhenius has found an empirical relation between the change of viscosity and the temperature of a pure liquid, as follows:[2]

$$\frac{d \log \eta V^{\frac{1}{2}}}{dT} = \frac{K_1}{T^2} \qquad (14)$$

where V is the volume of a gram of liquid of viscosity η, and K_1 is a constant, which for a given liquid is proportional to its boiling point on the absolute scale, as shown in the following table. The value of the quotient K_1/T_b for homologous series of compounds increases slightly with the boiling point, in the same way as does the constant of Trouton's rule.

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[1] Hosking, *Proc. Roy. Soc. N. S. Wales*, **43**, 37 (1909).

[2] Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.* **3**, No. 20 (1918); Thorpe, *Science Progress* **12**, 583 (1918).

For computing the viscosity of a liquid at one temperature from that at another temperature, the above equation is more useful in the integrated form:

$$(V^{1/2}) \log \left(\frac{\eta_1}{\eta_2}\right) = K_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{15}$$

K_1 may be obtained from Table 31.

TABLE 31.—VISCOSITIES AND ARRHENIUS' CONSTANTS

Substance	$10^5 \eta V^{1/2}$	$\frac{K}{T_b}$
Unsaturated hydrocarbons	233	1.002
Acetaldehyde	249	1.005
Paraffins	257	1.078
Ketones	270	1.074
Mercaptans	275	1.012
Iodides	277	1.073
Acid anhydrides	279	1.153
Esters	288	1.169
Monochlorides	296	1.129
Thiophene	341	1.243
Carbon tetrachloride	400	1.452
Water	290	1.800
Formic acid	507	1.800
Acetic acid	398	1.387
Propionic, butyric acids	342	1.322
Methyl alcohol	380	1.562
Allyl alcohol	483	2.507
Other primary alcohols	422	2.087
Secondary alcohols	552	3.066
Tertiary alcohols	579	3.784

The substances below the dotted line are believed to be associated into larger molecules in the liquid state, and hence give a large value of the coefficient K_1/T_b.

Certain substances (shown below the dotted line in Table 31) do not seem to conform to this rule; they are, for the most part, the substances which did not follow Trouton's rule, and which for other reasons are considered abnormal. But the relation between K_1 and the boiling point holds for such a variety of chemically unrelated substances as to indicate that the nature and constitution of the molecule are only subordinate in producing internal friction.

Arrhenius has also found that the absolute viscosity of a liquid at its boiling point is proportional to the square root of the density at this point, again for "normal" substances only. The value of $\eta.10^5/\sqrt{d}$ is about 250 for a large number of substances.

TABLE 32.—RELATION OF VISCOSITY TO DENSITY

Substance	$\eta.10^5$	d	$\eta.10^5/\sqrt{d}$
Pentane	200	0.5995	256
iso-Pentane	203	0.6057	261
Hexane	204	0.6103	261
Heptane	199	0.6144	254
Octane	198	0.6124	253
Acetaldehyde	219	0.773	249
Ether	205	0.695	246
Dipropyl ether	212	0.674	258
Methyl formate	312	0.957	319[a]
Ethyl formate	289	0.878	309[a]
Propyl formate	278	0.808	309[a]
Carbon bisulfide	305	1.222	276
Methyl sulfide	253	0.832	277
Benzene	316	0.809	350[b]
Thiophene	339	0.988	341[b]

[a] See the section on molecular association.

[b] Evidently there are occasional exceptions to the rule which are not to be explained by the formation of molecular aggregates larger than single molecules, as benzene is not considered an "associated" substance.

Viscosities of Mixtures.—The problem of expressing the viscosity of a mixture of liquids in terms of the properties of the pure substances is still an unsettled one. Egner[1] states that the expression

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2$$

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[1] *Medd. K. Vetenskapsakad. Nobelinst.* **3,** No. 22 (1918).

holds for mixtures, where x_1 and x_2 are the mol fractions of the two liquids; η_1 and η_2 are their viscosities. Kendall[1] states that the viscosities of mixtures are not any simple function of the per cent by weight, of the mol fraction, or of volume concentration, but he finds that for certain mixtures the formula above leads to results for mixtures which are only slightly lower than measured viscosities. This statement has been questioned,[2] since it applies only at a single temperature and is quite in error at temperatures higher than 25°. Bingham proposes that the best representation of viscosities in mixtures is

$$\frac{1}{\eta} = \frac{a}{\eta_1} + \frac{b}{\eta_2}$$

where a and b are the volume concentrations of the liquids present.

Molecular Association in The Liquid State.—In the preceding paragraphs mention has been made of abnormal substances, that is, substances which did not follow some particular rule, often an empirical one. These deviations are believed to indicate that in the liquid state the molecules are more or less strongly combined into double or triple molecules, held together by forces somewhat different from primary valence forces, and of a less specific character. There is evidence of such "association" into larger molecules or groups of molecules, derived from abnormalities in boiling points or vapor pressures, from volume changes on mixing liquids, from deviations from the rectilinear diameters of Cailletet and Mathias, from the compressibility of water, from the critical constants, from surface tension and from viscosity measurements.

When attempts are made to compute the extent of this association, whole numbers are seldom obtained, which indicates that the combination is never complete and that these numbers are averages. But when the degrees of complexity as determined by rival methods are compared, such wide discrepancies are observed that one questions whether any known method of measuring this association is reliable. In the appended table are shown the values of the association factor for a few substances by various methods. Thus Tyrer computes that water in the liquid state is $(H_2O)_{6.3}$ while Longinescu writes $(H_2O)_{4.6}$ and Bingham $(H_2O)_{2.2}$. The futility of quantitative discussion of this data is evident, but it should be said that most of the methods agree as to *which* liquids are considerably associated and which ones have nearly the normal molecular weight corresponding to the formula as usually written. The case of water has been studied more than that of any other liquid; the "association factor" is not found to be a whole number by any of the methods. Most authorities seem to agree that liquid water is largely a mixture of $(H_2O)_2$ and $(H_2O)_3$ in proportions which vary with the temperature.[1] There are also simple $(H_2O)_1$ molecules present, and these evaporate to give water vapor, which has nearly the normal molecular weight.

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[1] *J. Am. Chem. Soc.*, **39**, 1,787 (1917); Kendall and Wright, *J. Am. Chem. Soc.*, **42**, 1776 (1920); Kendall and Monroe, *J. Am. Chem. Soc.*, **43**, 115 (1921).

[2] Bingham and Sarver, *J. Am. Chem. Soc.*, **42**, 2,011 (1920).

Table 33 shows the number of simple molecules combined into a complex liquid molecule according to various authorities.

TABLE 33.—EXTENT OF MOLECULAR ASSOCIATION IN THE LIQUID STATE

Substance	Tyrer I[1]	Tyrer II	Ramsay and Shields[2]	Longinescu[3]	Batchinski[4]	Bingham[5]	Walden[6]	From volume relations[7]
Water	6.30	1,170	1.64 to 2.32	4.6	2.13 to 1.10	2.20	2.66 to 1.41	5.60
Acetic acid	2.00	2.02	2.77	1.7	2.74	1.73	1.8—2.8	4.74
Formic acid	2.70	....	3.13	1.8	2.68	....	3	
Methyl alcohol	2.55	3.51	3.24 to 2.20	3.2	3.43	1.79	2.2—3.2	3.81
Ethyl alcohol	1.89	2.90	2.43	2.1	3.65	1.74	2.0—3.2	5.37
Acetone	....	1.13	1 26	...	2.74	1.23	1.2—1.5	....

[1] *J. Phys. Chem.*, **19**, 81 (1915).
[2] From surface tension measurements.
[3] *J. chimie physique*, **6**, 552 (1908).
[4] From critical constants.
[5] *Am. Chem. J.*, **43**, 287 (1910).
[6] *Z. physik. Chem.*, **65**, 257 (1908).
[7] *Z. physik. Chem.*, **80**, 50 (1912).

Arrangement of Molecules in Liquid Surfaces.—Marcelin[2] discovered that when a liquid fatty acid is placed upon water, it spreads rapidly over the surface until a certain definite area is reached, after which it does not tend to spread further. The phenomenon has been studied thoroughly by Langmuir,[1] who measured the area covered by very small quantities of oils of known composition. A weighed quantity of fatty acid of high molecular weight, and insoluble in water, was dissolved in a large volume of benzene; a weighed drop of this dilute solution was placed on the water surface. The benzene soon evaporated and left a quantity of oil far smaller than it would be possible to weigh directly, but of accurately known weight. The oil film was pressed against the end of a rectangular tray containing the water on which the oil was floating, and its area was carefully measured. Many experiments showed that the area was directly proportional to the quantity of oil; demonstrating that the spreading took place only to a certain definite limit in every case.

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[1] A full discussion of the case of water will be found in *Trans. Faraday Soc.*, **6**, 71–123 (1910): the whole subject has been treated by W. E. S. Turner in a monograph in the Findlay series of text books.

[2] *Ann. Physik.*, **1**, 19 (1914).

The explanation of the limited spreading is as follows. There is no great attraction of the water for the oil molecules as a whole, as this would manifest itself as a solubility of the oil *in* the water, whereas the oil remains *on* it and does not enter the water phase as a whole. The acids consist of two parts, the —COOH group and an oily hydrocarbon chain. Now the —COOH group is attracted by water, as shown by the solubility of the lower organic acids in water, and as would be expected since the group would then find itself in a medium containing hydroxyl groups such as it contains. But the fatty part is, like all hydrocarbons, only slightly soluble in water and but little attracted by water. Langmuir states that when oleic acid, for example, is placed upon water, the carboxyl groups do *actually dissolve in the water*, that is, they combine with it by secondary valence forces, and the fatty chain remaining outside of the water. By spreading the oil as a *monomolecular* layer, all of the carboxyl groups enter the water without causing the hydrocarbon chains to separate from one another. Further spreading, however, would bring water molecules into the surface between the hydrocarbon chains and separate them. The attraction of the hydrocarbon part for molecules of its own kind prevents this and the spreading ceases.

From the weight of oil employed, its molecular weight and

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[1] *J. Am. Chem. Soc.*, **39**, 1,848 (1917); *Proc. Nat. Acad. Sci.* **3**, 2 51 (1917).

Avogadro's number, the number of molecules in a film of known area was readily calculated, and from this the cross section of a single molecule was calculated. It will be seen from Table 34 that the area is the same for all of the acids having a single hydrocarbon chain. The case of tristearin indicates that the $C_3H_5\equiv$ group has dissolved in the water layer, leaving three hydrocarbon chains in the oil surface, since the area per molecule is three times that of a single chain. On account of the double bond in oleic acid, this substance appears to be bent double in its chain, and triolein occupies six times the surface of a single chain. The fact that the area per molecule for the first three acids in the table is the same indicates that the chains are standing on end and projecting into the oil layer, and that the carboxyl group is dissolved in the water layer. The square root of this molecular area thus gives the diameter of the hydrocarbon chain, which is of the same order of magnitude as the molecular diameters calculated at the end of Chapter II. Since the thickness of the oil film is then the length of the hydrocarbon chain, it is easy to calculate the length of chain per carbon atom; this also is seen to be of the order of 10^{-8} centimeters, similar to the diameters calculated for small gaseous molecules.

TABLE 34.—MOLECULAR DIMENSIONS CALCULATED FROM THE SPREADING OF OIL FILMS ON WATER

Substance	Molecular cross-section Sq. Cm.	Molecular Diameter = $\sqrt{\text{Cross-Sec.}}$ Cm.	Length of Molecule = thickness of oil film	Length per Carbon atom in the Chain
Palmitic acid, $C_{15}H_{31}COOH$	21×10^{-16}	4.6×10^{-8}	24.0×10^{-8}	1.5×10^{-8}
Stearic acid, $C_{17}H_{35}COOH$	22	4.7	25.0	1.39
Cerotic acid, $C_{25}H_{51}COOH$	25	5.0	31.0	1.20
Tristearin $(C_{18}H_{35}O_2)_3C_3H_5$	66	8.1	25.0	1.32
Oleic acid, $C_{17}H_{33}COOH$	46	6.8	11.2	0.62
Triolein $(C_{18}H_{33}O_2)_3C_3H_5$	126	11.2	13.0	0.69
Myricyl alcohol, $C_{30}H_{61}OH$	27	5.2	41.0	1.37

Similar views as to the structure of surfaces have been developed independently by Harkins[1] from a study of the decrease in free surface energy which takes place when two liquid surfaces are brought together. The active groups, such as —COOH,

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[1] *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).

=CO, —CN, —OH, or —CONH$_2$, strive to enter the water. If the hydrocarbon chain attached to such a group is not too large, it can be dragged into water by the active group, and the compound will be soluble in water to a greater or less extent, depending upon the quantity of insoluble hydrocarbon chain in the molecule. If the hydrocarbon tail is too large, it cannot be brought into the water by the attraction exerted on the active group, and two liquid phases result. The active ends still enter the water, however, and give rise to the surface structure already explained.

When a liquid is in contact with its vapor, the molecules in the surface layer so arrange themselves that the least active portion of the molecule is toward the vapor phase. At any interface between phases the molecules so arrange themselves that the passage from one phase to the other will be as little abrupt as possible. It is this molecular orientation which sets up at the surfaces of liquids and solids the so-called electric double layer. The stability of emulsoid particles also seems to depend upon this surface arrangement; the best emulsifying agents are long-chain compounds with a highly active group on one end of the molecule, such as soaps.

Questions

1. The heat of vaporization of water at its boiling point is 538 cal. per gram. Calculate the vapor pressure of water at 80°, and the percentage error of the calculated pressure. Refer to Table 27 for the necessary vapor pressure at 80°.

2. The vapor pressure of benzene is 548 mm. at 70° and 755 mm. at 80°. (*a*) Calculate the quantity of heat required to vaporize a gram of benzene. (*b*) Calculate the vapor pressure of benzene at 90°. *Ans.* 96 cal., 1,008 mm.

3. Calculate the value of Trouton's constant, L/T for several typical liquids in Table 29, and tabulate them. What is a possible explanation of the variations in the case of liquids whose constants are over 20.3? What liquids show the largest deviations from Trouton's rule? What types of liquids conform to it most closely?

4. Calculate the molal latent heat of vaporization for water, ethyl alcohol, benzol, pentane, ammonia, carbon dioxide, and oxygen by means of the modifications of Trouton's rule, and compare the errors of these calculations with those from the simple Trouton rule. Refer to Table 29 for the data.

5. The viscosity of water at 25° is 0.00893. Calculate its viscosity at 100° by the integrated Arrhenius equation, using the data of Table 31. The measured value is 0.00284.

6. Calculate from the simple gas law the density of acetic acid at its critical temperature and pressure, 321° and 57 atmospheres. Apply Young's ratio to determine whether acetic acid is associated in the liquid state.

7. Calculate the vapor pressure of alcohol at 90°, using the data given in Table 29.

8. Calculate the area which would be covered by a milligram of oleic acid, $C_{17}H_{33}COOH$, when allowed to spread upon a water surface.

9. The densities of liquid ammonia and saturated ammonia vapor are as follows:

TEMPERATURE	LIQUID DENSITY	VAPOR DENSITY
98.75	0.4640	0.0533
109.25	0.4339	0.0691
116.4	0.4056	0.0873
121.3	0.3831	0.1024
123.2	0.3750	0.1085
125.45	0.3584	0.1220
129.6	0.3246	0.1509

Plot the density of each phase against the temperature, and determine from this plot the critical temperature and critical density of ammonia, using the law of rectilinear diameters. (A. Berthoud, *Helvetica Chimica Acta*, 1, 84 (1918).)

10. Benzol has a surface tension of 28.88 dynes at 20°. What is the diameter of a capillary tube in which benzene rises 1 centimeter? How high would water rise in the same tube?

$m - \frac{n_0}{\sqrt{1 - \frac{v^2}{c^2}}}$

CHAPTER IV

SOLID SUBSTANCES

The most important characteristics of the solid state are rigidity, and a definite arrangement of the atoms or molecules of a crystal with reference to one another. It has long been known that the forces acting between constituent atoms of solid substances were specific in character, and of great magnitude. In general there is no tendency for a substance in crystallizing from its melt or from solution to include the molecules of other substances; and this affords a ready means of purification of the products of chemical operations. Certain chemically related substances have the property of forming mixed crystals; in these cases recrystallization is not a suitable method of purification, and other means suited to the problem in hand must be employed.

The changes in properties attending the passage of a substance from liquid to solid are much smaller than those which attend the condensation of a gas. The density of a solid is commonly within 10 per cent of that of its liquid, while the density of a liquid is often a thousand times that of the vapor from which it was formed. Solids have vapor pressures, just as liquids have; they increase with increasing temperature as in the case of liquids. The rate at which the vapor pressure, or sublimation pressure, changes with temperature may be calculated from the Clausius-Clapeyron equation; but since the change in state is from solid to vapor, the heat term is the sublimation heat of the solid. The equation is

$$\frac{dp}{dT} = \frac{L_s}{T\Delta v} = \frac{pL_s}{RT^2}$$

where L_s is the molecular latent heat of sublimation, and the vapor formed has the volume RT/p.

The **melting point** of a substance is that temperature at which its liquid and solid phases are in equilibrium under a pressure of 1 atmosphere. As the presence of some other substance lowers the melting point in proportion to the quantity of it present, an accurate determination of melting point is a ready means of establishing the purity of a product.

Changes of pressure have but slight effect upon the melting point of a solid, except where very high pressures are involved. For example, an increase of 2,100 atmospheres lowers the melting point of ice 22°. The effect of pressure can be calculated from the Clausius-Clapeyron equation,

$$\frac{dp}{dT} = \frac{L_f}{T\Delta v}$$

where Δv is the increase of volume which takes place on melting, and L_f is the heat of fusion. Here the approximate form of this equation obtained from the ideal gas law cannot of course be applied. If the effect of pressure is desired in degrees per atmosphere, Δv should be expressed in cubic centimeters, and L_f in cubic-centimeter-atmospheres. One calorie is equivalent to 41.24 c.c. atmospheres. For example, the heat absorbed during the melting of a gram of water is 79 cal., the increase in volume upon melting is -0.09 c.c., whence

$$\frac{dp}{dT} = \frac{79 \times 41.24}{-0.09 \times 273} = -132$$

atmospheres per degree, which corresponds to $\frac{1}{-132} = -0.0076$ degrees per atmosphere. The negative sign indicates that pressure lowers the melting point of ice.

By considering the kinetic energy of the molecules of solids, and their energy of vibration, Honda[1] has derived an approximate relation between the heat of fusion and absolute melting point, which is somewhat similar to Trouton's rule for liquids. The rule is restricted to elements alone, and states that the atomic heat of fusion in small calories is two times the absolute melting point. The rule holds roughly for several metals, but is greatly in error for many others, indicating that the true relation between latent heat and melting point has not yet been discovered. Thus the quotient of L/T is 4.8 for bromine and chlorine, 3.3 for tin, 4.7 for bismuth, 3.8 for iodine, etc., but between 1.9 and 2.6 for most metals of high melting point.

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[1] *Physical Review*, **12**, 425 (1918).

Heat Capacity of Solids.—Two simple laws express the heat capacities of substances near room temperature; the first refers to elements, the second to compounds. The law of Dulong and Petit states that the product of specific heat and atomic weight (that is, atomic heat capacity) is about 6.2 for all of the solid elements at constant pressure. Elements of atomic weight less than 40 appear to be exceptions to the rule. It has been found[1] that the atomic heat capacity at constant volume is more nearly constant for all elements than that at constant pressure, for when the heating is carried out at constant volume there is no work of expansion done against the internal forces which hold a solid together. The atomic heat at constant volume is 5.9 cal. A comparison of these two rules is given in Table 35, where all of

TABLE 35.—HEAT CAPACITIES OF THE ELEMENTS

Element	Atomic heat at constant volume, C_v	Atomic heat at constant pressure, C_p
Sodium	6.4	6.9
Magnesium	5.8	6.0
Aluminum	5.7	5.8
Potassium	6.5	7.1
Iron	5.9	6.0
Nickel	5.9	6.1
Copper	5.6	5.8
Zinc	5.6	6.0
Palladium	5.9	6.1
Silver	5.8	6.1
Cadmium	5.9	6.2
Tin	6.1	6.4
Antimony	5.9	6.0
Iodine	6.0	6.9
Platinum	5.9	6.1
Gold	5.9	6.2
Thallium	6.1	6.4
Lead	5.9	6.3
Bismuth	6.2	6.3
Average	5.9	6.2

The average deviation of C_v from 5.9 is only half as large as the average deviation of C_p from 6.2.

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[1] Lewis, *J. Am. Chem. Soc.*, **29**, 1,165 (1907).

the data refer to room temperatures. As explained in a later section, all of these heat capacities decrease rapidly at low temperatures, and increase slightly for higher temperatures.

Several elements, notably those of low atomic weight, are exceptions to these rules, they have much smaller atomic heat capacities than heavier elements. For example, some of these atomic heat capacities are sulfur 5.5, phosphorus 5.6, carbon 1.6 (diamond) to 1.9 (graphite), boron 2.5, silicon 4.8, aluminum 5.7.

Kopp's law states that the molecular heat capacity of a solid compound is the sum of the atomic heat capacities of the elements composing it; the elements having atomic heat capacities lower than those required by the law of Dulong and Petit retain these lower values in their compounds. The heat capacity of an atomic weight of oxygen in a solid compound is naturally not the same as that of an atomic weight of gaseous oxygen at the same temperature; it is the difference between the formal heat capacity of a metal oxide and the atomic heat of the metal contained in it. The average heat capacity of oxygen so obtained is 4.0 cal. per atomic weight; the atomic heat capacity of hydrogen in its solid compounds is 2.3 cal. For example, the molecular heat of carborundum, SiC, is 6.4, that calculated from Kopp's law is 4.8 + 1.8 = 6.6; the measured value for lead sulfide is 12.2, the calculated one 6.2 + 5.5 = 11.7, for sodium chloride the measured value is 12.8, the calculated one 13.1. This illustrates the agreement generally obtained by the application of this law; some further examples are shown in Table 36.

TABLE 36.—HEAT CAPACITIES AND KOPP'S LAW OF ADDITIVE ATOMIC HEATS

Substance	Molecular heat capacity		Per cent error	Substance	Molecular heat capacity		Per cent error
	Measured	Kopp's law			Measured	Kopp's law	
$PbCl_2$	18.50	18.6	0.5	PbI_2	19.60	20.1	3
NaCl	12.80	13.1	2	PbS	11.70	12.2	4
AgCl	13.04	12.3	5	KI	13.60	14.0	3
TlCl	12.60	12.4	2	AgI	13.45	13.0	3
$ZnCl_2$	18.55	18.4	1	$CaCO_3$	20.20	20.0	0.5
				SiC	6.40	6.6	3

Heat Capacity and Temperature.—When the investigations on heat capacities of solids were extended to low temperatures it was found that the law of Dulong and Petit failed completely, and that at the very lowest temperatures the specific heats of all substances became very small and approached zero. Similarly, at higher temperatures many elements showed atomic heat capacities considerably greater than 6.2. Some data on the atomic heats of elements at low temperatures are given in Table 37 and shown in Fig. 15. It will be noted that in the neighborhood of 300° absolute, which is about room temperature, most of the elements conform to the law of Dulong and Petit, that is, have atomic heat capacities of about six. At lower temperatures this heat capacity decreases much more rapidly for some elements than for others. Thus at 100° absolute, about the temperature of liquid air, potassium and lead still have nearly their normal heat capacities, while those of copper and aluminum have decreased to half of the former values. All of the curves point toward zero heat capacity as the absolute zero of temperature is approached, all of them show at the lowest temperatures a

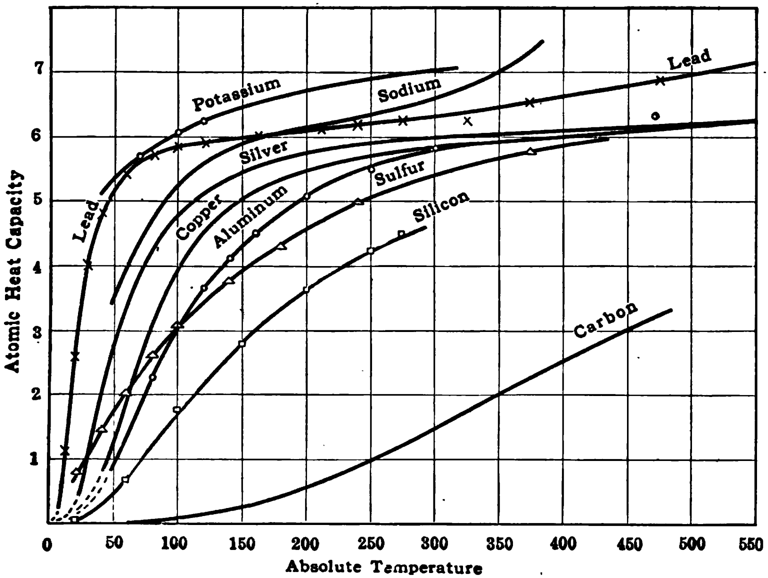

FIG. 15.—Change of atomic heat capacity with temperature.

convex curvature toward the temperature axis, followed by a change of curvature at higher temperatures, then a portion which is nearly horizontal. This suggests that the heat capacity of all substance must be expressed by the same form of equation, with a different constant or set of constants for each element. Einstein derived an equation which took as a characteristic constant the vibration frequency of the atoms of the element, assuming that there was one such frequency for each kind of atom. The equation was shown to be considerably in error, and was altered by Nernst and Lindemann,[1] who assumed that there was also a vibration of the atoms with a frequency half that of the characteristic one. This frequency is calculated from the melting

TABLE 37.—ATOMIC HEAT CAPACITIES OF THE ELEMENTS[2] AT VARIOUS TEMPERATURES

Absolute temperature	Al	C	Cu	Pb	S	K	Si	Ag	Na
20	0.07	0.00	0.11	2.62	0.79	....	0.03	0.39	....
40	0.53	0.00	0.81	4.82	1.46	....	0.25	2.00	....
60	1.43	0.018	1.90	5.43	2.05	....	0.68	3.37	4.01
80	2.30	0.048	2.98	5.73	2.60	....	1.25	4.22	4.77
100	3.01	0.084	3.94	5.86	3.08	6.04	1.78	4.76	5.27
120	3.64	0.144	4.58	5.91	3.45	6.24	....	5.12	5.61
140	4.12	0.222	4.93	5.96	3.77	6.36	2.60	5.37	5.82
160	4.53	0.330	5.15	6.01	4.07	6.48	....	5.55	5.93
180	4.84	0.456	5.30	6.05	4.31	6.60	....	5.67	6.05
200	5.10	0.594	5.43	6.10	4.55	6.70	3.62	5.77	6.14
220	5.29	0.750	5.55	6.15	4.76	6.77	....	5.86	6.26
240	5.45	0.924	5.65	6.20	4.99	6.84	4.14	5.92	6.35
260	5.58	1.116	5.73	6.25	5.19	6.92	....	5.95	6.39
273	5.64	1.236	5.78	6.28	5.24	6.98	4.53	6.00	6.53
298	5.74	1.45	5.83	6.31	5.40	7.04	....	6.02	6.66
323	5.84	1.83	5.88	6.34	....	....	....	6.04	6.85
373	6.04	2.24	5.98	6.51	5.98	....	....	6.08	7.40
473	6.34	3.24	6.14	6.88	....	....	....	6.14	....

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[1] *Z. Elektrochem.*, **17**, 817 (1911).

[2] The data are from the following sources: Griffiths, *Proc. Roy. Soc. London*, (*A*) **90**, 557 (1914); Eastman and Rodebush, *J. Am. Chem. Soc.*, **41**, 489 (1919); Keesom and Onnes, *Comm. Phys. Lab. Leiden*, **147a**, (1915); Mills, *J. Phys. Chem.*, **21**, 359 (1917); Schübel, *Z. anorg. Chem.*, **87**, 81 (1914).

point of the element, from its compressibility, or from the spectrum of the light reflected from it. The calculations of heat capacity are laborious and not always satisfactory, but they do show the general shape of the specific heat curve.

A better equation has been derived by Debye,[1] assuming that the atoms vibrate with all frequencies from zero to a certain maximum number. This equation is also very complicated, but for high temperatures it reduces to the simple form $C_v = 3\ R$, and for very low temperatures it becomes

$$C_v = 77.94 \times 3R \left(\frac{T}{\theta}\right)^3$$

where θ is proportional to the maximum vibration frequency. The heat capacity at low temperature is thus proportional to the third power of the absolute temperature; the dotted portions of the curves of Fig. 15 are of the right shape to correspond with this fact.

Much still remains to be done upon the problem of heat capacity however. Thus the atomic heats of sodium, potassium and magnesium tend toward much higher values than the $3R$ predicted by Debye's equation,[2] and the elements iron, nickel, cobalt, bismuth, tin and chromium do not approach $3R$ as an upper limit of their atomic heat capacities,[3] but aluminum, copper, silver, zinc and cadmium do approach such a limit. No adequate explanation suited to all of these cases has yet been found.

Forces Acting Between Atoms.—The great tensile strength and the slight compressibility of metals are incompatible with the older idea that solids are composed of hard particles (molecules) separated by considerable spaces. Richards[4] has studied carefully the changes in volume which accompany the formation of compounds, and from the magnitude of these changes (they were always decreases in volume) he concludes that the atoms themselves are compressed during combination. Now it is known that the pressures required to compress elementary solid substances are enormous; since the chemical reaction produced these compressions, the forces there operating must also be very large. In Table 38 are given the sums of the atomic volumes of the reacting elements, the volume of a mol of alkali chloride, the decrease in volume accompanying the combination, the part of this decrease due to the compression of the alkali element alone, (the compression of an atomic weight of chlorine was 12.5 c.c.), and the pressure in atmospheres which would be required to produce the same change in volume in the alkali element.

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[1] *Annalen der Physik.*, **39**, 789 (1913).

[2] Lewis, *Proc. Nat. Acad. Sci.*, **4**, 25 (1918).

[3] Schübel, *Z. anorgan. Chem.*, **87**, 89 (1914).

[4] *J. Am. Chem. Soc.*, **36**, 2,417 (1914); and earlier papers.

TABLE 38

Substance	Volume of metal plus chlorine	Molal volume of salt formed	Contraction during formation of compound	Part of contraction due to metal	Pressure which would cause same contraction. atm.
Lithium chloride	38.1	20.5	17.6	5.1	43,000
Sodium chloride	48.7	27.2	21.5	9.0	24,000
Potassium chloride	70.4	37.3	33.1	20.6	14,000
Rubidium chloride	80.8	44.0	36.8	24.3	10,500
Caesium chloride	96.0	42.4	53.6	41.1	9,500

This compression is brought about by *chemical* forces, that is, the forces holding the atoms of solids in their positions, and it is seen that these forces are of great magnitude.

Arrangement of Atoms in Crystals.—The regular arrangement of the faces and angles of a crystal suggests that there is some definite way of packing together the molecules or atoms which make up the crystal. This regularity of crystalline form is independent of the size of crystal, hence it must be due to a unit of packing repeated over and over again throughout the whole crystal. Recently the work on reflection of X-rays from crystal faces[1] has established definitely the true nature and structure of this unit. The wave length of visible light has been determined from interference figures produced by a ruled grating which acts as a mirror for the light; where the spacing of lines in the grating is made of the same order as the wave length of light. The wave length of X-rays is about 10^{-8} centimeters., and it will be remembered that the molecular diameters mentioned in the preceding chapters are also of this order. Hence it is possible for the planes of atoms in a crystal to serve as a grating which would produce interference of X-rays, and it was a successful application of this idea which formed the basis of Bragg's determinations. In the face of a crystal of sodium chloride there are both sodium atoms and chlorine atoms, also in the layers beneath the surface; and the two atomic species are present in equal numbers. There is, however, a fundamental difference between a reflecting grating for visible light and the "reflection" of X-rays from a crystal face, in that the latter rays penetrate deep into the layers of atoms within the crystal itself. Hence if the spacings between the atomic layers were not absolutely uniform there could be no interference when the beam was reflected at a particular angle, but only a steady reflection at all angles. The existence of such angles at which there was interference is thus proof that the layers have an absolutely uniform spacing. As the wave length of these rays is only a thousandth of that of the shortest visible light, it is necessary to study the reflection photographically, or by means of the effect of the rays as shown by an electroscope.

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[1] Bragg, *X-rays and Crystal Structure*, (G. Bell and Sons, London 1916).

From experiments with X-rays of known wave length it was thus determined that in a crystal of rock salt the planes of atoms are 2.81×10^{-8} centimeters apart. Since the power of an atom to reflect X-rays is proportional to its weight, a study of the reflected ray thus serves to determine the relative position of each atom in the crystal. In this way it was shown that the *atoms* of sodium and of chlorine alternate in a salt crystal along three sets of lines perpendicular to each other and spaced at 2.81×10^{-8} centimeters. They take up positions at the corners of a cubical unit which is repeated throughout the crystal, as shown in Fig. 16. Each sodium atom is there surrounded by six chlorine atoms equidistant from it, and each chlorine is surrounded by six sodium atoms. It is of course impossible to say to which chlorine any particular sodium atom belongs, and the identity of the molecule is wholly lost in the crystal. Thus the whole crystal is a single large structure or "molecule"[1] which is held together by the forces acting between chlorine atoms and sodium atoms; that is, by strictly *chemical* forces.

Spatial arrangements have already been worked out for over

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[1] Langmuir, *J. Am. Chem. Soc.*, **38**, 2,221 (1916).

30 substances,[1] and the number is being increased rapidly by many investigators who have taken up this line of work. Sodium chloride, sodium bromide, potassium chloride and potassium bromide all have structures in which the atoms are arranged in a simple cubic lattice like that of sodium chloride shown in Fig. 16.

The diamond consists of two interpenetrating lattices, in each of which the carbon atoms are at the corners of the elementary cubes, and in addition there is a carbon atom in the center of each face. This is called a face-centered cubic lattice, each carbon atom from one lattice is then surrounded by four other equidistant ones from the second lattice, forming a regular tetrahedron around it. The distance between atomic centers is 1.52 × 10^{-8} centimeters.

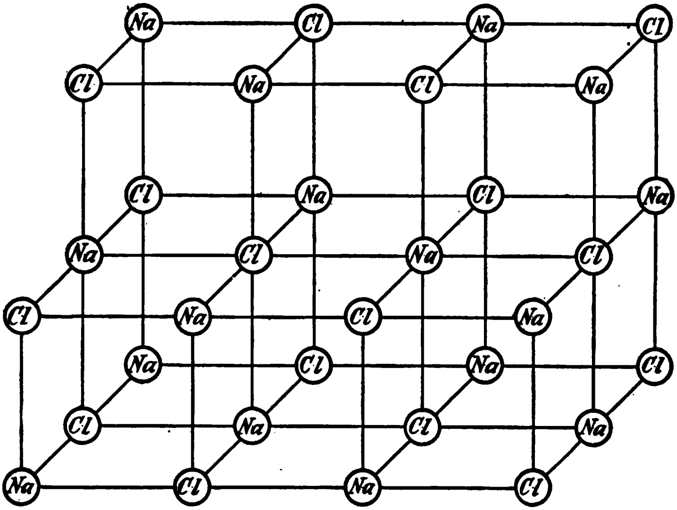

FIG. 16.—Arrangement of atoms in a crystal of sodium chloride.

The structure of carborundum[2] is very similar to that of diamond; silicon atoms replacing half of the carbon atoms. The distance between atomic planes is 2.179 × 10^{-8} centimeters, from which the volume of the group CSi containing 1 atom of each element is $(2.179 \times 10^{-8})^3$ or 20.7×10^{-24} cubic centimeters. From Avogadro's number and the atomic weights of carbon and silicon it may be calculated that the weight of this atomic group CSi is $(12.0 + 28.3) / (6.0 \times 10^{23}) = 65.5 \times 10^{-24}$; and it follows that the quotient $65.5/20.7 = 3.11$ should be the density of carborundum if this atomic group is close-packed throughout the crystal. The observed density of carborundum is 3.12, a satisfactory agreement. It should be noted that the atomic distances (assuming the atoms to be in contact in a crystal) so obtained are of the order of 10^{-8} centimeters, which is in agreement with the other methods of calculating atomic diameters. Crystals of organic substances have not been successfully investigated as yet, largely on account of the small reflecting power of hydrogen atoms, due to their slight mass. It may be found that the lattice consists of molecules in organic substances, but this has not been determined at present.

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[1] An excellent book describing the work on this subject has been written by Bragg and his son, in which will be found details of the analysis of crystalline structure. Photographs of atom models will be found in *Nature*, **105**, 646 (1920); see also Bragg, *Science Progress* **15**, 367 (1921).

[2] Burdick, *J. Am. Chem. Soc.*, **40**, 1,749 (1918).

If, in place of employing a crystalline substance as a grating, a beam of X-rays is passed *through* the crystal[1] and the emerging beam is photographed, it will be found that there is a diffraction pattern which is characteristic of the substance used; the diffractions being closely connected with the spacing of the internal atomic planes and the atoms composing them. A small quantity of the powdered crystalline substance may be used in place of a single large crystal, in which case the photographic film is a narrow strip forming a cylinder whose axis passes through the powdered material.

Chemical Analysis by X-rays.—When X-rays of a single wave-length are passed through a tube of the finely divided (powdered) crystals, a line will appear on the film corresponding to every important plane of atoms in the specimen used. If this is a single pure substance only a few lines will be found; if it is a mixture of substances, many lines are formed. This has been made[2] the basis of a method of quantitative analysis which promises to be of great usefulness. In a mixture of substances, each one gives its characteristic pattern and the relative intensities of the individual patterns are proportional to the quantities of the substances in the mixture. Substances of similar crystal structure will give similar patterns, which however differ in the magnification or "spread" of the pattern. Thus lithium, sodium and potassium fluorides, sodium and potassium chlorides and magnesium oxide all have exactly the same arrangement of atoms in their crystals, and give patterns of precisely similar lines; the magnifications of which are inversely proportional to the cube roots of their molecular volumes. Since no two substances have exactly the same molecular volumes, there is no danger of confusing them in an analysis of this kind, especially as the differences are greatly magnified in lines far from the center of the film. Since the interplanar distances are strictly characteristic of the *crystals*, this method of analysis shows the state of combination of the elements, that is, whether a mixture is sodium chloride and potassium fluoride or sodium fluoride and potassium chloride.

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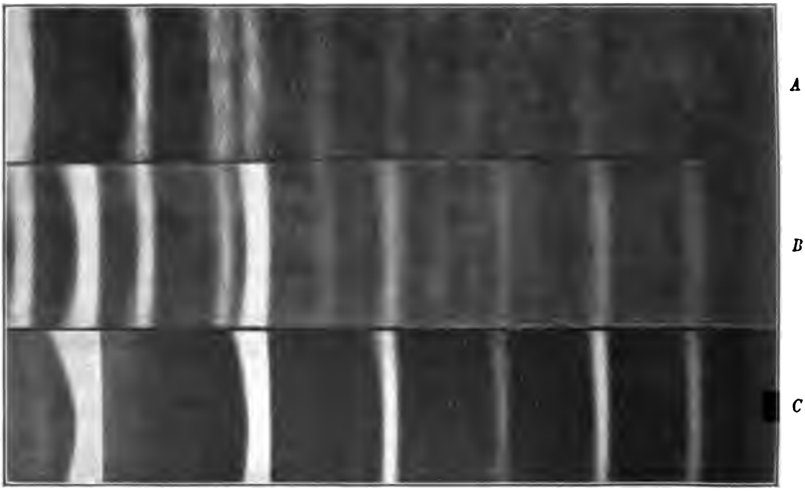
[1] Laue, *Sitzb. kgl. Bay. Akad. Wiss.*, **1912.**

[2] Hull, *J. Am. Chem. Soc.*, **41,** 1,168 (1919).



A. Pure $NaHF_2$. *B*. Sample for analysis. *C*. Pure NaF.
FIG. 17.—X-ray patterns of sodium fluoride and sodium hydrogen fluoride.

A single example will be shown to illustrate this method of analysis. In Fig. 17 are shown photographs[1] of the diffraction patterns of pure sodium fluoride, of a "sample" and of pure sodium-hydrogen fluoride. All of the lines in the sample which do not correspond to one of these pure substances correspond to the other, which shows that only these two salts are present in considerable quantity. By prolonging the exposure, faint lines from traces of impurity can be brought out and identified from their resemblance to photographs of pure substances. A cubic millimeter of substance is sufficient for a complete analysis, and the material is not altered in any way while its composition is being determined.

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[1] Courtesy of Dr. A. W. Hull of the General Electric Co.

Arrangement of Atoms in Metals.—Extension of X-ray analysis to powdered substances has been used to determine the arrangement of atoms in the metals[1] and other substances which cannot be prepared in large single crystals suitable for measurement by the Bragg method. The most common arrangement of atoms in metallic crystals is the face-centered cubic, which is obtained by dividing the space in a crystal into closely packed cubes and placing an atom at each cube corner and at the center of each cube face. This arrangement is also called cubic close packing, and is one of the two alternative arrangements that hard spheres of equal size assume when closely packed by pressure and shaking. The metals which have this arrangement of atoms in their crystals are aluminum, nickel, copper, rhodium, silver, platinum, gold and lead. The second type of arrangement in metals is the cube centered arrangement, with an atom at each cube corner and at each cube center of the elementary cubes. The atoms so arranged are not as closely packed as in the face-centered cubic arrangement, and this arrangement is not stable for spheres, which indicates either that the atoms of these elements are not spheres or that they are held in position by special types of forces. Lithium, sodium, chromium, iron, molybdenum and tungsten conform to this second type. The third type of arrangement for metals is obtained by dividing the space into equal closely packed right triangular prisms, the bases of which are equilateral triangles, and the altitudes 1.633 times the side of the triangles. An atom is located at each prism corner and at half of the prism centers. This is the second alternative arrangement assumed by equal spheres under pressure and shaking, and is the form shown by magnesium,[2] zinc, and cadmium. The simple cubic arrangement is not shown by metals, but is confined to salts with equal numbers of positive and negative atoms, such as the alkali halides and magnesium oxide. This arrangement is unstable for spheres, but stable for cubes. The tetrahedral arrangement, in which each atom is surrounded by four others arranged in a regular tetrahedron, is found in the diamond, carborundum, silicon, and in ammonium chloride.

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[1] Hull, *Proc. Am. Inst. Elec. Eng.*, **38**, 1,171 (1919); *Science*, **52**, 227 (1920).

[2] *Proc. Nat. Acad. Sci.*, **3**, 470 (1917).

X-ray methods have already been applied to the detection of flaws in steel, to determine the extent of crystallization in a metal specimen, to detect "blow-holes" in metal castings, cracks in metallic parts, and faults in lumber. Applications to other problems may be expected to appear frequently, especially in metallography, where the crystal structure of a specimen has such an important bearing on its mechanical properties.[1]

Structure of Surfaces.—From the arrangement of atoms in alkali halide crystals, it was seen that the identity of the molecules in them is lost; that the chemical attraction of an atom was equally distributed among the four or six surrounding atoms, to no one of which it was specifically "combined," it was equidistant from these atoms and equally "belonging" to each one. Of course as the atoms evaporate from the crystal they must do so in the requisite pairs or groups to form gaseous molecules. In other words, while molecules do definitely exist in the gaseous state and in solutions, they appear to lose their existence as separate individuals in a crystal. The question occurs at once, what about atoms in the surface? Since in a crystal the chemical attractions act in all directions, the surface atoms must either have the attractions normally exerted in the outward direction bent in some interior direction and there satisfied; or else this attraction exists unsatisfied, and there is extending out into space (for the molecular distance of 10^{-8} centimeters at least) a definite chemical attraction. The latter view is correct. For when a crystal is suspended in a saturated solution of it, the crystal will attach to itself other layers and grow in size. This could hardly be the case if the attraction of the outside layers of atoms in a crystal were fully satisfied, and it therefore seems certain that there is at a solid surface some unsatisfied chemical attraction, capable of holding (more loosely than in strict chemical combination perhaps) other molecules on the surface.

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[1] A detailed discussion of the applications of X-rays is given in the *Transactions of the Faraday Soc.*, **15**, Feb., 1920. Here the experimental methods are reviewed and explained, and interesting examples of the results are given. See also W. L. Bragg, *Nature*, **105**, 646 (1920).

Adsorption.—This is a term now commonly used to denote the formation of layers of molecules attached to or attracted by a solid surface of some other material, in contrast to the *absorption* of a substance into the interior of another. Thus the layer of gas which adheres so strongly to glass surfaces[1] is considered to be adsorbed; the coloring matter dissolved in sugar sirups is adsorbed by charcoal, and impurities in air and water are removed by adsorption on charcoal filters. The structure of surfaces as outlined in the previous paragraph affords a ready explanation of this; for the residual chemical affinity of the atoms in the surface layer holds the molecules of the adsorbed substance. All of the chemical attraction of the atoms in a surface is not free to adsorb other molecules, since part of it is exerted upon the atoms near it in the solid, but the active portion of this force is purely chemical. Adsorption is thus a species of chemical combination in a somewhat more loose way than that of the usual chemical reaction.

If this is the true explanation of adsorption, there would form a layer of gaseous molecules possibly one molecule deep. But the formation of a second layer would be possible only through the attraction of the gas molecules in the first layer for more molecules of their same kind. This would, in effect, be the formation of a condensed (*i.e.*, liquid) layer of the gaseous molecules; which we should not expect if the gas were far from its condensation pressure and temperature. Langmuir states that the forces involved in adsorption (chemical forces) of gaseous molecules on solid surfaces are very much larger than the forces acting between the molecules of liquids. If this is true, we should not expect the formation of a second layer of adsorbed gas, for this could be held only by the forces acting between molecules of the gas. Further, adsorption takes place from very dilute gases, where the forces of attraction between molecules are known to be negligibly small. The formation of a layer one molecule deep is thus analogous to the spreading of oil films on water into a layer one molecule deep.

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[1] Langmuir, *J. Am. Chem. Soc.*, **40**, 1,361 (1918).

The forces holding an adsorbed *molecule* are of the same nature as those holding together the *atoms* of crystals; thus whether adsorption will take place or not, and to what extent, depends on the magnitude of these forces, *i.e.*, the residual valence of the atoms in the adsorbed molecules. Such forces are typically chemical, and exhibit all the differences in intensity and quality characteristic of chemical forces.

No satisfactory equation has yet been developed for expressing the quantity of substance adsorbed on a given surface as a function of its pressure or concentration. The best known attempt in this direction is the equation of Freundlich,[1]

$$q = a\,p^{1/n}$$

where q is the quantity of adsorbed substance, a is the proportionality constant, p is the pressure of the adsorbed substance, and n is a constant greater than unity, but different for different surfaces and gases. This equation is the best of the many proposed to cover adsorption, and is satisfactory as an interpolation formula. But it fails to fit the facts when applied over a wide range of pressure. At low pressures the adsorption might well be expected to be proportional to the pressure (that is, to the

TABLE 39.—ADSORPTION OF NITROGEN ON MICA AT 90° ABSOLUTE

Pressure (dynes per square centimeter)	Mols adsorbed × 10^6	Calculated from Freundlich equation	Per cent deviation of Freundlich equation
34.0	1.37	1.54	+11
23.8	1.28	1.31	+ 3
17.3	1.17	1.04	− 3
13.0	1.06	1.01	− 5
9.5	0.995	0.883	−12
7.4	0.90	0.795	−11
6.1	0.79	0.726	− 7
5.0	0.707	0.68	− 4
4.0	0.628	0.62	− 1
3.4	0.556	0.58	+ 4
2.8	0.500	0.536	+ 7

The calculated values were obtained from the equation $q_F = 8.4p^{0.417}$. At the lowest pressure the slope of the plot (log p against log q) corresponded to $1/n = 0.68$; at higher pressures it decreases to $1/n = 0.20$.

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[1] *Kapillarchemie*, 1909.

number of molecules striking the surface), while as the pressure is increased the surface layer approaches saturation and there is no further increase of adsorption because there is no more residual attraction of the solid surface.

Table 39 shows the measured quantity of nitrogen adsorbed on a surface of mica, and the calculated adsorption, using Freundlich's equation. The constants of this equation are evaluated from a plot of the observations, choosing values which cause the equation to fit the data as well as possible.

Liquid Crystals.—Certain substances of complex organic nature melt to a turbid liquid having quite different properties from those of ordinary liquids. As the temperature is further raised, a point is reached at which this melt changes sharply to a clear liquid of ordinary properties. The substance thus shows, in addition to its usual "melting point," another transition temperature at which it assumes the properties of liquids. While in this intermediate state the liquid exhibits double refraction, a property characteristic of crystalline substances. When a beam of light passes through a doubly refracting substance, there are two emerging beams, only one of which follows the ordinary laws of refraction, and the rays are polarized. This occurrence is characteristic of substances which are not isotropic, that is, whose properties are not the same when measured in different directions. It follows that the intermediate "liquid" state is one in which the properties of the liquid are not the same in all directions. Lehmann[1] calls this intermediate condition the "liquid-crystalline" state; perhaps a better name would be doubly-refracting liquids. Apparently weak forces such as those acting in crystals are at work arranging the molecules in a kind of space lattice similar to that of crystals but less definite in character. The sharp disappearance of this double refraction at a definite temperature bears a resemblance to the melting point of crystals, except that in this case the substance is already fluid.

An early explanation of liquid crystals (Nernst, Bose) was that there were molecular swarms containing several atoms, but this idea has been found inadequate to explain the observations.

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[1] A review of his very numerous papers on this subject is given in *Physikalische Zeitschrift*, **19**, 73 (1918).

Born[1] and Voigt[2] both consider that in liquid crystals there is an arrangement of the *molecules* in some particular way, perhaps parallel to one another with respect to some one axis, and that this is responsible for the behavior of liquids in this peculiar state. They do not say that there is definitely a space lattice similar to that in solid substances, but that if there is such a lattice, it differs sharply from the one found in solids, in that it consists of molecules, not atoms. The identity of the molecules, which is lost in crystals, is assumed when they melt to form liquid crystals. At the second transition point, or clearing point, this molecular lattice is lost, and with it the double refraction characteristic of anisotropic substances.

Over 170 substances showing two transition points[3] have been prepared, and from a study of them it has been shown that there is no space lattice detectable by the usual X-ray methods applicable to solid substances. These liquid crystals have optical rotatory powers as high as 4,000° for a film 1 mm. thick; a quartz plate of this thickness has a rotation of only about 25°. There is apparently no relation between the constitution of the compounds[4] and their capacity for producing liquid crystals. It may be that all organic substances are capable of forming

TABLE 40.—SUBSTANCES FORMING LIQUID CRYSTALS[5]

Substance	Transition temperatures, degrees		Range of existence of liquid crystals, degrees
Cholesterin benzoate	145	179	24
p-Azoxyanisole	118	136	18
p-Azoxyphenetole	134	169	35
Pyridine nitrate	88	105	17
Quinoline nitrate	102	119	17
p-Methylaminobenzaldehyde phenyl hydrazone	170	190	20
p-Ethylaminobenzaldehyde phenyl hydrazone	160	181	21

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[1] *Sitzb. kgl. preuss. Akad.*, **1916**, 614.

[2] *Physikalische Zeit.*, **17**, 76, 152 (1917).

[3] *Engineering*, **106**, 349 (1918), a review of the subject.

[4] Chaudhari, *Chemical News*, **117**, 269 (1918).

[5] Rotarski, *Berichte*, **41**, 1,994 (1908).

liquid crystals, but the temperature ranges of their existence are so small that they have escaped detection. This is rendered unlikely by the fact that some of the substances exhibit their peculiar properties through a range of 35°. A few examples are mentioned in Table 40.

Questions

1. The melting point of monoclinic sulfur is 110° and it increases 0.05° per atmosphere. The density of monoclinic sulfur is 1.960 and its heat of fusion is 320 cal. per atomic weight. Calculate the density of liquid sulfur.

2. At 0° the specific volume of ice is 1.091, that of water may be taken as 1.000. When a gram of ice melts 79 cal. are absorbed. How much does an increase of 1 atmosphere alter the melting point of ice? Is this an increase or decrease?

3. The vapor pressure of ice is 4.58 mm. at 0° and 3.30 mm. at – 4°. Calculate the heat of sublimation of a gram of ice from the approximate form of the Clausius-Clapeyron equation.

4. Calculate the specific heat of ice from Kopps' law. Calculate the specific heat of iron oxide, and the percentage error. The measured specific heats are 0.54 and 0.16 respectively.

5. The sublimation pressure of bromine is 15.7 mm. at – 21°; and 25 mm. at –15.5°. Calculate the latent heat of sublimation of bromine. Calculate from this value the sublimation pressure at –11°.

Ans. 60.7 cal. per gram; 35 mm.

6. Calculate the density of sodium chloride from the atomic spacing given in the text. The actual density is 2.17.

CHAPTER V

SOLUTIONS

A solution is a homogeneous phase in which two or more molecular species are present. We shall consider in this chapter only liquid solutions, that is, mixtures of two liquids or a liquid in which a gas or a solid has been dissolved, or dispersed into single molecules. So-called "colloidal solutions" contain molecular groups or aggregates which are very much larger than single molecules; they are in fact exceedingly fine suspensions of solids or liquids, and are considered later in a separate chapter. "Solid solutions" will be considered briefly under heterogeneous equilibrium; solutions of ionized substances are considered in the next chapter.

There are no fixed rules by which to predict whether a substance will dissolve in a given liquid or not, or to what extent. The probability that a solution can be formed increases with the resemblance of the solvent to the dissolved substance; hence most closely related liquids mix with one another in all proportions.. Chemically unlike substances such as water and silver nitrate or sodium chloride also form solutions over a wide range of compositions; yet silver chloride scarcely dissolves in water at all. Carbon bisulfide is soluble in all proportions in alcohol, but very slightly soluble in water; though water and alcohol are soluble in one another in all proportions.

In dilute solutions one of the components of the mixture is present in large excess and is called the *solvent;* the dissolved substance being called the *solute.* It is convenient to express the composition of these solutions in terms of the number of mols or formula weights of solute present per liter of solution (volume concentration) or per thousand grams of solvent. The compositions of more concentrated solutions are expressed by mol fractions, as was done in mixtures of gases. The mol fraction of a substance in solution is the number of molecular weights of it divided by the number of molecular weights of all substances present. An example will make this clearer. A solution containing 10 per cent by weight of alcohol ($C_2H_5OH = 46.00$) has a density of 0.9839. A liter of this solution weighs 983.9 grams and contains 98.39 grams or $\frac{98.39}{46.00} = 2.14$ mols of alcohol. It contains also 885.5 grams or $\frac{885.5}{18} = 49.4$ molecular weights of water; the mol fraction of alcohol is $\frac{2.14}{2.14 + 49.4} = 0.0416$. Similarly the mol fraction of the water is 0.9584, since the mol fractions of all the substances present must add to unity.

Ideal Solutions.—Certain substances form solutions whose properties may be expressed in terms of the mol fractions of the components and the properties of the pure substances by means of simple laws. These solutions are called "ideal solutions," and the laws expressing their properties in terms of the properties of the constituents are called the laws of ideal solutions. The volume of an ideal solution is equal to the sum of the volumes of the substances forming it; there is no heat evolved upon mixing the constituents; and the constituents of an ideal solution are able to dissolve in one another in all proportions. These statements may be regarded as a definition of an ideal solution. Most of the solutions encountered in chemistry are not strictly ideal solutions, and they are not, therefore, described accurately by the simple laws of ideal solutions; but for practical purposes many such solutions can be treated as ideal solutions, and their properties calculated in terms of those of the constituents. Just what is meant by "practical purposes" will depend upon the accuracy desired in the calculation. In treating the laws of ideal solutions we shall endeavor to form an opinion as to the deviations to be expected from the various types of solution, and of the limitations of the laws stated. Failure to appreciate that these laws have limited applicability will often lead to considerable errors; thus the vapor pressure of a solution of a mol of alcohol in a mol of water as calculated from the laws of ideal solutions is in error by 30 per cent.

Vapor Pressure of Solutions. Raoult's Law.—The vapor pressure of a solution is commonly understood to mean the partial pressure of solvent vapor above the solution, but in case more than one constituent of the solution is volatile, each one has a partial pressure in the vapor over the solution. Addition of a solute to a solvent lowers the total vapor pressure of the solution in case the solute is not volatile. This lowering is proportional to the mol fraction of the added solute in an ideal solution, or the vapor pressure itself is proportional to the mol fraction of the solvent. Expressed in the form of equations, these two statements of Raoult's law (which are two ways of saying exactly the same thing) are as follows:

$$\frac{p_0 - p}{p_0} = x \text{ and } p = p_0 x_0 = p_0(1 - x), \tag{1}$$

where p_0 is the vapor pressure of pure solvent, and x_0 is its mol fraction in the solution: p is the vapor pressure of solvent from the solution, and x is the mol fraction of the solute. The *fractional* lowering of the vapor pressure is the same at all temperatures for a given solution, and is a measure of the mol fraction of the dissolved substance. In applying Raoult's law the vapor pressure of solvent and solution must always be determined at the same temperature.

Raoult's law offers a means of determining the molecular weights of dissolved substances from vapor pressure lowering of solutions of known composition. In Tables 41 and 42 are given the vapor pressures of some solutions, together with the molecular weight of the solute calculated from Raoult's law. Table 43 shows the vapor pressure lowering per mol of

TABLE 41.—LOWERING OF VAPOR PRESSURE
Naphthalene (formula weight 128) dissolved in benzene at 75°

Grams solute	Grams solvent	Mols solvent	Vapor pressure in millimeters	Molecular weight calculated
0.0000	26.53	0.340	639.85	
0.7913	26.53	0.340	628.7	131.3
1.3141	26.53	0.340	621.6	131.7
1.8411	26.53	0.340	614.5	131.3
2.3446	26.53	0.340	607.4	129.2
3.3453	26.53	0.340	594.3	128.5

Rosanoff and Dunphy, *J. Am. Chem. Soc.*, **36**, 1,416 (1914).

TABLE 42.—BENZIL (FORMULA WEIGHT 210) DISSOLVED IN ETHYL ALCOHOL AT 15°

Grams solute	Grams solvent	Mols solvent	Vapor pressure in millimeters	Molecular weight calculated
1.300	46.00	1	31.982	210
0.711	46.00	1	32.061	191
0.367	46.00	1	32.121	200
0.196	46.00	1	32.150	214
0.000	46.00	1	32.180	

Tower and Germann, *J. Am. Chem. Soc.*, **36**, 2,449 (1914).

TABLE 43.—SOLUTIONS OF MANNITE IN WATER AT 20°

Molal concentration per 1,000 grams water	Vapor pressure lowering		Per cent deviation of Raoult's law	Lowering per mol of solute (observed)
	Observed	Calculated from Raoult's law		
0.0984	0.0307	0.0311	1.3	0.3113
0.1977	0.0614	0.0622	1.3	0.3108
0.2962	0.0922	0.0931	1.0	0.3123
0.3945	0.1227	0.1239	1.0	0.3107
0.4938	0.1536	0.1547	0.7	0.3111
0.5944	0.1860	0.1858	0.1	0.3129
0.6934	0.2162	0.2164	0.1	0.3118
0.7927	0.2478	0.2469	0.3	0.3126
0.8922	0.2792	0.2775	0.7	0.3129
0.9908	0.3096	0.3076	0.6	0.3124

Frazer, Lovelace and Rogers, *J. Am. Chem. Soc.*, **42**, 1,793 (1920).

solute in 1,000 grams of water. The vapor pressure lowering, expressed in terms of the weights of substances in solution, is

$$\frac{p_0 - p}{p_0} = x = \frac{m/M}{m/M + m'/M'}, \tag{2}$$

where m is the weight of solute added to m' grams of solvent, M is the molecular weight of the dissolved substance and M' is the molecular weight of the solvent. It will be seen that the agreement is all that could be desired.

Direct measurements of vapor pressure are more difficult, from an experimental point of view, than are certain other measurements (freezing point depressions, boiling points) which are equivalent to vapor pressures. These will generally be found more useful in molecular weight determinations than vapor pressure measurements.

Raoult's law applies strictly to dilute solutions, but does not accurately express the vapor pressure of most concentrated solutions in terms of the mol fraction of solute. Conversely the mol fraction calculated from vapor pressure measurements in strong solutions is unreliable. The following data will serve to illustrate the errors when concentrated solutions are involved.

TABLE 44.—VAPOR PRESSURE OF SUGAR SOLUTIONS AT 30°

Mols sugar per 1,000 grams water	Mol fraction of solute	Vapor pressure (millimeters)	$\frac{p_0 - p}{p_0} = x$	Per cent error in mol fraction calculated from Raoult's law
0.993	0.0175	31.22	0.0194	10
1.65	0.0288	30.76	0.0338	13
2.38	0.0410	30.21	0.0520	21
3.27	0.0555	29.43	0.0746	25
4.12	0.0690	28.72	0.0980	29
5.35	0.0877	27.55	0.1326	33
6.36	0.1025	26.70	0.1612	37

Berkley and Hartley, *Trans. Roy. Soc. London A*, **218**, 295 (1919).

Doubtless much of this error is due to combination of some sort between the sugar and water; perhaps the molecular weight of liquid water is not 18. But at least these factors also exert an influence in other cases as well, so that the deviations here found may be considered typical of strong solutions.

Vapor Pressure of the Solute. Henry's Law.—The solubility of a gas at a given temperature is proportional to the pressure of the gas above the solution. Expressed as a vapor pressure law, this states that the partial pressure of a volatile solute from a solution is proportional to its mol fraction, or to its concentration. The equations are

$$p = kx \text{ or } p = k'C, \qquad (3)$$

where p is the partial pressure of the gas above the solution, x is its mol fraction and C its concentration in the solution. It will be seen that this law closely resembles Raoult's law, the only difference being that the proportionality constant is not the vapor pressure of the pure gas in the equation for Henry's law. The value of the constants k and k' must be determined at each temperature by experiment; these constants are not the same for different solutes, or for the same solute at different temperatures or for various solvents. Henry's law is useful, therefore, only in calculating the solubility at some new pressure, or the vapor pressure of the solute at some new concentration, when the corresponding quantity is known for one solution at the temperature in question. Data illustrating this law are given in Table 45.

TABLE 45.—SOLUBILITY OF CARBON DIOXIDE IN WATER

At 100°			At 25°		
Pressure of CO_2 (atmospheres)	Molal concentration[1]	p/C	Pressure of CO_2 (atmospheres)	Molal concentration[2]	p/C
60	0.303	198	4.12	0.139	29.7
70	0.342	205	5.33	0.180	29.7
80	0.374	213	7.64	0.258	29.6
90	0.427	211	10.61	0.358	29.6
100	0.461	218	12.16	0.410	29.6
110	0.503	218	19.73	0.666	29.6
120	0.554	217	22.56	0.761	29.6
130	0.606	215	40.61	1.370	29.6
140	0.661	212			
150	0.695	216			
160	0.748	214			
170	0.770	221			

Distribution Between Phases.—It will be seen from Henry's law that the ratio of the quantity of solute per liter of solution to the quantity of gas per liter above the solution is a constant, since the concentration in the gas phase is proportional to the pressure. This same conclusion has been found to apply to the ratio between the equilibrium concentration of solute in one liquid phase and that in another liquid phase in contact with it. For example, if a substance soluble in both water and benzene is dissolved in water, and this solution is shaken with a quantity of benzene, it will be found at equilibrium that the ratio of the molal concentration in the benzene layer to that in the water layer is a constant, regardless of the quantity of solute used, or of the relative quantities of benzene and water. Like the constant in Henry's law, the distribution constant must be determined by experiment for each solute and for each pair of mutually insoluble liquids, and the constant changes with the temperature. When two phases are in equilibrium with one another as regards some particular component and one of these is in equilibrium with a third phase, the other is also in equilibrium with this third phase. If the third phase is the solid solute itself, then when one liquid is saturated with the solid and in equilibrium with another liquid, this second liquid must also be a saturated solution of the solute. Thus the distribution constant for a given substance between two solvents is the ratio of the solubilities of that substance in the two phases, provided the distribution law holds for such concentrated solutions. Like Raoult's law and Henry's law, the distribution law is exact for very dilute solutions, and exhibits deviations in more concentrated ones. When the solutions (except those of ionized substances) are less than one formal, the deviations from these laws are usually less than two per cent.

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[1] Sander, *Z. physikalische Chemie*, **78**, 513 (1911).

[2] Smith, *J. Am. Chem. Soc.*, **40**, 885 (1918).

Table 46 shows the distribution of succinic acid between water and ether, expressed as the mol fraction of the acid in each phase. The distribution law applies only to a particular species of molecule, and would not give a constant if succinic acid were in a different condition in the two phases, for example if it were associated into double molecules in the ether layer, or if it were highly ionized in the water layer. When a set of distribution ratios calculated from experimental data shows a steady decrease or increase with the concentration, the most common explanation is the assumption of a different molecular condition by the solute in the two phases. Usually this is an association into double molecules in organic liquids containing no oxygen when the solute is an organic acid. The constant distribution ratio in Table 46 shows that succinic acid does not polymerize in ether solution, and does not ionize to any considerable extent in water solution. It will be noted that the distribution ratio for ammonia is not constant for concentrations much above normal. This is in harmony with the deviations of other laws in concentrated solutions. The distribution ratio of acetic acid between water and benzene changes rapidly with the concentration, as acetic acid forms double molecules in the latter solvent.

The distribution equation in terms of mol fractions and in terms of concentrations is

$$\frac{x_1}{x_2} = k' \quad \text{or} \quad \frac{C_1}{C_2} = k, \tag{4}$$

where the subscripts refer to the two phases involved.

All three of the laws just considered, Raoult's law, Henry's law, and the distribution law, refer to the distribution of some one molecular species between two phases. Thus, Raoult's law states that the concentration of the *solvent* molecules above a solution is proportional to their concentration in the solution; Henry's law says that the concentration of *solute* molecules above a solution is proportional to the concentration in it; and the distribution law refers to the ratio of the concentration of *solute* in two liquid phases in equilibrium with one another.

TABLE 46.—DISTRIBUTION OF SUCCINIC ACID BETWEEN WATER AND ETHER

(Concentrations are in mols of acid per 100 mols of solution)

15°			20°			25°		
Water layer	Ether layer	k	Water layer	Ether layer	k	Water layer	Ether layer	k
0.372	0.305	1.223	0.2025	0.1535	1.322	0.364	0.248	1.471
0.440	0.358	1.229	0.431	0.319	1.351	0.720	0.485	1.485
0.575	0.468	1.228	0.495	0.366	1.353	1.088	0.727	1.493
0.880	0.714	1.233	0.629	0.465	1.355	1.513	0.731	1.489
0.963	0.778	1.237	0.936	0.686	1.364			
.....	.....	.....	1.211	0.889	1.363			

Forbes and Coolidge, *J. Am. Chem. Soc.*, **41**, 150 (1919).

TABLE 47.—DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM

At low concentration			At high concentration		
Concentration in water	Concentration in chloroform	C_w/C_c	Concentration in water	Concentration in chloroform	C_w/C_c
0.0443	0.00165	26.2	1.02	0.045	22.7
0.0220	0.00091	24.1	3.13	0.146	21.4
0.0110	0.00044	24.7	5.24	0.283	18.5
0.00572	0.00021	25.7	7.29	0.457	15.9
0.00275	0.00011	24.6	9.35	0.710	13.2
			12.25	1.227	10.0

Z. physik. Chem. **30,** 258 (1899). *J. Am. Chem. Soc.*, **33,** 940 (1911).

TABLE 48.—DISTRIBUTION OF ACETIC ACID BETWEEN BENZENE AND WATER AT 25° (Acetic acid forms double molecules in benzene)

C_B	C_w	C_B/C_w
0.0159	0.579	0.0274
0.0554	1.382	0.0401
0.2250	3.299	0.0776
0.9053	6.997	0.1290

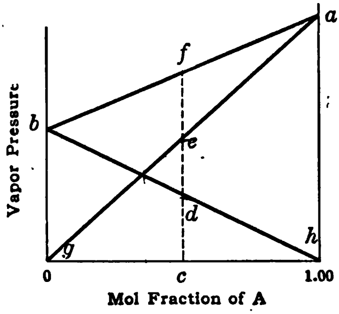

FIG. 18.

Vapor Pressures of Ideal Solutions of Two Liquids.—When two liquids, *A* and *B*, form an ideal solution, the partial pressure of each in the vapor is proportional to its mol fraction in the solution, and these partial pressures may be calculated from Raoult's law. Thus

$$p = p_0x \text{ and } p' = p_0'x'$$

where p_0 is the vapor pressure of pure liquid *A* and x is its mol fraction in the solution; and p_0' is the vapor pressure of pure liquid *B* and x' is its mol fraction. The vapor pressures over the whole range of mol fractions from pure *A* to pure *B* for such an ideal solution are shown in Fig. 18, where the partial pressure of *A* is given by the line *ga*, that of *B* by *bh*, and the total vapor pressure (which is the sum of the two partial vapor pressures) by the line *ba*.

When the solution contains only A, $x = 1$, $x' = 0$, and the total pressure is p_0, the vapor pressure of pure A (*ah* in the figure). Similarly for pure B, $x = 0$, $x' = 1$ and the total pressure is p' (*bg*). When the substances are present mol for mol, $x = 0.5$, $x' = 0.5$, $p = 0.5p_0$; and $p' = 0.5p_0'$, corresponding to *ce* and *cd* respectively. The total pressure is the sum of these pressures, or *cf*. If *ce* and *cd* are the partial pressures, then the mol fractions in the vapor are $X_A = ce/cf$ and $X_B = cd/cf$; and these will be the mol fractions of the two substances in the first portion of distillate condensed from the solution at this temperature, since distillate is condensed vapor. As *ce* and *cd* are not equal, the mol fraction of constituent A in this vapor will not be the same as in the solution from which it came. In general, the greater the difference between the vapor pressures of the two components, the greater the difference in composition between a liquid and a vapor in equilibrium with it.

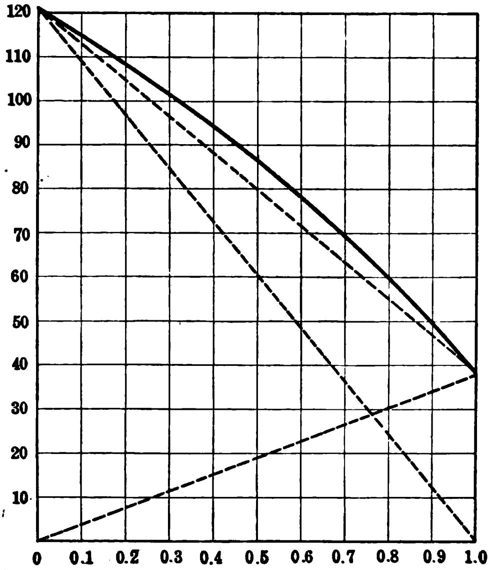

FIG. 19.

Ideal solutions of this kind are formed only when the two components are chemically very similar. For most pairs of liquids which mix in all proportions the deviations from ideal solutions are considerable when both constituents are present in large proportion, for example when the mol fractions are between 0.1 and 0.9 for both. This may be due to the formation of complexes (double or triple molecules) which render the mol fractions calculated from the composition by weight in error. The vapor pressures of mixtures of benzene and toluene are given in Table 49 and Fig. 19, together with the total vapor pressure calculated from the sum of the partial pressures demanded by Raoult's law.

[illegible]

TABLE 49.—VAPOR PRESSURES OF MIXTURES OF BENZENE AND TOLUENE AT 30°

Mol fraction of toluene in solution	Exptl. total pressure	Calculated partial pressures		Calculated total pressure	Per cent error
		Benzene	Toluene		
0.00	121.8	121.8	....	121.8	....
0.10	115.1	109.5	3.8	113.3	2
0.20	108.3	97.4	7.6	105.0	3
0.30	101.4	85.3	11.3	96.6	5
0.40	94.0	73.1	15.1	88.2	6
0.50	86.0	60.9	18.9	79.8	7
0.60	77.8	48.7	22.6	71.3	8
0.70	69.2	36.5	26.4	62.9	9
0.80	60.0	24.4	30.1	54.5	9
0.90	50.1	12.2	33.9	46.1	8
1.00	37.7	....	37.7	37.7	....

Schulze, *Annalen der Physik*, **59**, 82 (1919).

As the two components are chemically very similar, there is every reason to expect approximate agreement with the laws of ideal solutions, and this may be taken as a good example of the agreement generally obtained.

Benzene and carbon disulfide form a solution which deviates somewhat more from an ideal one. The total vapor pressure at 30°, and the partial pressures of each substance from solution are shown in Table 50. The total pressure was measured with a manometer, and each partial pressure was computed from the mol fraction of it in a small portion of distillate collected.

TABLE 50.—VAPOR PRESSURES OF SOLUTIONS OF BENZENE AND CARBON DISULFIDE[1] AT 30°

Mol fraction of benzene in solution, 30°	Total vapor pressure in millimeters	Partial pressure of benzene millimeters	Partial pressure of CS_2 millimeters	Pressure of CS_2 calculated from Raoult's law	Per cent deviation
0.00	434.6	.....	434.6	......	
0.0800	413.1	14.7	398.4	399	0
0.2286	378.9	35.8	343.1	335	2.5
0.3723	340.8	53.3	287.5	272.5	5
0.6516	259.1	81.6	177.5	151	15
0.8845	169.5	107.3	62.2	50	19
1.000	119.3	119.3			

The large errors in the pressure of carbon disulfide calculated by means of Raoult's law when it is present in small proportion illustrate an important fact. Raoult's law is a law for the vapor pressure of a solvent, and carbon disulfide is scarcely the solvent when its mol fraction is only $1 - 0.885 = 0.115$, as it is in the next to last line of the table. If the vapor pressure of *benzene* from this solution is calculated from Raoult's law, it is $119.3 \times 0.8845 = 105.5$, which is in error by about 2 per cent.

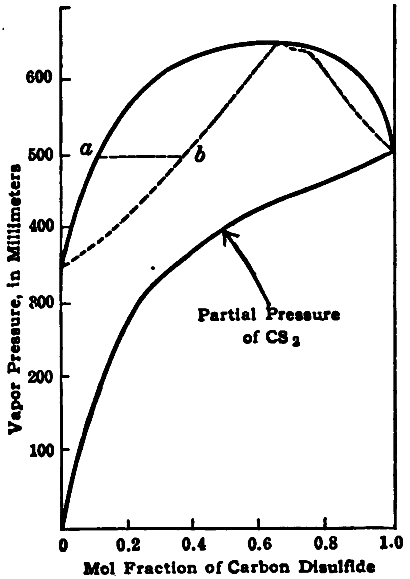

FIG. 20.—Acetone–CS_2 mixtures at 35°.

Mixtures of acetone and carbon bisulfide[2] may be taken as an extreme example of the deviations of Raoult's law. Here the total vapor pressure of an equi-molal solution is far higher than that of either pure component, and the partial pressure of carbon bisulfide from this solution is 20 per cent higher than that calculated from Raoult's law. For these solutions no simple laws are known. The composition of vapor in equilibrium with each solution is shown by the dotted line below the total vapor pressure curve. For example, the solution whose composition is *a*, Fig. 20, is in equilibrium with vapor of composition *b*.

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[1] Sameshima, *J. Am. Chem. Soc.*, **40**, 1,503 (1918).

[2] Zawidski, *Z. physik. Chem.*, **35**, 172 (1900).

Constant Temperature Distillation.—By reference to the fourth line of Table 50 it will be seen that the partial pressures of benzene and of carbon disulfide are respectively 53.3 and 287.5 mm. over a solution in which the mol fraction of benzene is 0.3723. The partial pressures in the vapor phase are proportional to their mol fractions in the vapor (Dalton's law), each pressure being the product of the mol fraction and the total pressure. Hence the mol fractions in the vapor phase are $53.3/(53.3 + 287.5) = 0.156$ for benzene and 0.844 for carbon disulfide. If this vapor is cooled so that it condenses completely, the mol fractions in the condensed liquid will be the same as in the vapor from which it is formed, 0.156 and 0.844. This is exactly what happens in distillation; a vapor is expelled from a solution, and in this vapor the constituents are present in the ratio of their vapor pressures over the solution; this vapor condenses to a liquid having the same composition as the vapor, but a different composition from the solution out of which it was distilled.

Of course if the whole solution were distilled, the total distillate would have the same composition as the original solution. But the *first portion* of distillate is richer in carbon disulfide than the original solution, and the liquid remaining behind will be richer in benzene. In Table 51 are given the mol fractions of benzene in the vapor over each of the solutions of Table 50; it will be seen that each distillate contains a smaller proportion of benzene than the liquid from which it was expelled. The dotted line of

TABLE 51.—BENZENE AND CARBON DISULFIDE AT 30°

Mol fraction benzene in solution	Partial pressure benzene, millimeters	Partial pressure CS_2, millimeters	Mol fraction benzene in vapor
0.0800	14.7	398.4	0.0355
0.2286	35.8	343.1	0.0945
0.3723	53.3	287.5	0.1564
0.6516	81.6	177.5	0.3151
0.8845	107.3	62.2	0.6333

Fig. 21 is so drawn that each point on it shows the composition of vapor in equilibrium with the solution whose composition is shown by the solid line horizontally across from it. Thus a solution in which the mol fraction of benzene is 0.6 has a vapor pressure shown by *c*, and gives a vapor whose composition is shown by *c′*, about 30 mol per cent benzene; and this vapor condenses to a liquid of the same composition.

We have so far assumed a constant temperature of 30° for the fractional distillation, and let the total pressure be whatever it might. In practice the pressure is kept constant, usually at 1 atmosphere, and the solution is brought to this total pressure by raising the temperature until the solution boils. This will be considered after the boiling of solutions containing only one volatile component has been presented.

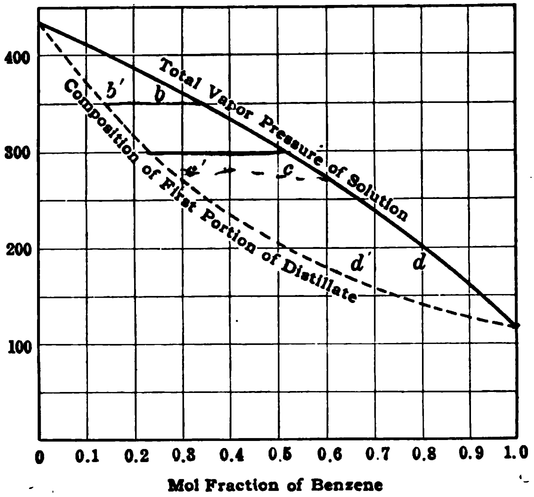

FIG. 21.—Benzene and CS_2 at 30°.

Boiling Point of Solutions.—The boiling point of any liquid or solution is the temperature at which the total vapor pressure is equal to that of the atmosphere, 760 mm. of mercury. Solutions, like pure liquids, increase their vapor pressures as the temperature is raised, but at any given temperature (for example at the boiling point of the solvent) the vapor pressure of a solution is less than that of the pure solvent. The vapor pressure lowering is proportional to the mol fraction of the dissolved substance, as indicated by Raoult's law. It will therefore be necessary to heat a solution to a temperature above the boiling point of the solvent before its vapor pressure becomes 1 atmosphere, in case the solute has no vapor pressure. A diagram of these conditions near the boiling point of a solution is given in Fig. 22; the solid line represents the vapor pressure of pure solvent and the dotted line the vapor pressure of a solution in which the mol fraction of the non-volatile solute is x.

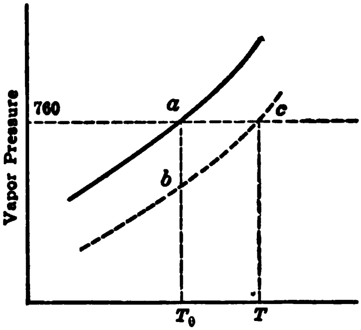

FIG. 22.

The vapor pressure of the solution at T_o, the boiling point of the solvent, is less than 760 mm. by the distance ab; to bring the pressure up to 760, so that the solution can boil, the temperature must be raised (while the vapor pressure increases along the dotted line) until the point c is reached, at the temperature T. The relation between the lowering of the vapor pressure and the boiling point raising is $ab/ac = (p_o - p)/(T - T_o)$. But ab/ac is the slope of the dotted line, that is, it is the rate of change of the vapor pressure of the solution with the temperature. It will be seen that the dotted and solid lines are nearly parallel however, at least for the short distances involved in a small change of boiling point, and hence we may write dp_o/dT for $\frac{ab}{ac}$, in place of dp/dT; that is, employ the change of vapor pressure of the pure solvent with the temperature in place of the change in vapor pressure of the solution with the temperature. Then we may write

$$\frac{p_o - p}{T - T_o} = \frac{dp_o}{dT} = \frac{p_o x}{T - T_o} \tag{5}$$

by substituting for $p_o - p$ its value $p_o x$ from Raoult's law on page 113. On solving this equation for the elevation of the boiling point, ΔT_b, we have

$$T - T_o = \frac{p_o x}{dp_o/dT} \quad \text{or} \quad \Delta T_b = kx, \tag{6}$$

since the terms p_o and dp_o/dT are characteristic of the solvent.

The value of k will not be the same for all solvents, but must be determined in one of the ways explained below. The validity of this equation is illustrated by solutions of diphenyl in benzene.[1] Two pieces of boiling point apparatus, like that shown in Fig. 23, were used, one of which contained pure benzene and the other the solution. The boiling points of the solvent and solution were determined at the same moment, thus avoiding any error due to a change of atmospheric pressure during the progress of an experiment. The results for several solutions are shown in Table 52.

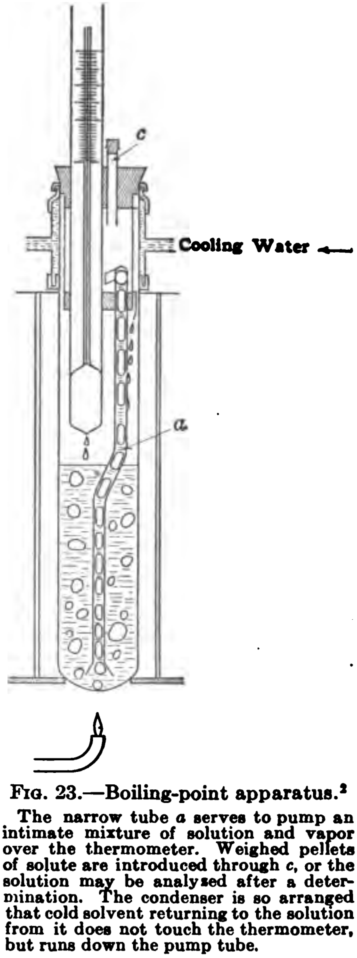

FIG. 23.—Boiling-point apparatus.[2]

The narrow tube a serves to pump an intimate mixture of solution and vapor over the thermometer. Weighed pellets of solute are introduced through c, or the solution may be analysed after a determination. The condenser is so arranged that cold solvent returning to the solution from it does not touch the thermometer, but runs down the pump tube.

In laboratory practice, the composition of a solution is commonly expressed in terms of the mols of solute per 1,000 grams of solvent, and the elevation of the boiling point produced by a mol of solute in 1,000 grams of solvent is called the *molal elevation of the boiling point, B*. For example, 1,000 grams of water is 1000/18 or 55.5 mols of water, and when a mol of solute is dissolved in 1,000 grams of water its mol fraction is $x = 1/(1 + 55.5) = 0.0177$. The vapor pressure of water at its boiling point changes at the rate of 0.0358 atmospheres per degree, whence from equation (6), $p_o = 1$, $dp_o/dT = 0.0358$, and

$$\Delta T_b = \frac{0.0177}{0.0358} = 0.495^\circ$$

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[1] Washburn and Read, *J. Am. Chem. Soc.*, **41**, 729 (1919).

[2] Cottrell, *J. Am. Chem. Soc.* **41,** 721 (1919).

TABLE 52.—SOLUTIONS OF DIPHENYL IN BENZENE

Boiling point elevation	Mol fraction solute exptl.	Mol fraction solute calculated	$\frac{\Delta T}{x} = k$	Per cent error
1.333	0.0380	0.0387	35.7	1.8
1.709	0.0490	0.0494	35.0	0.7
2.152	0.0613	0.0618	35.1	0.8
2.521	0.0718	0.0717	35.0	0.1
3.142	0.0890	0.0885	35.3	0.5

for a solution of a mol of solvent in 1,000 grams of water. In this calculation water vapor has been assumed an ideal gas; if correction is made for its deviation from the laws of an ideal gas, the molal elevation becomes 0.518°. Then the boiling point of any aqueous solution of a non-volatile substance is

$$\Delta T_b = 0.518C = BC \tag{7}$$

where C is the concentration of the solution in mols per 1,000 grams. The values of this constant B for several liquids are given in Table 53. It will be seen that this equation furnishes a convenient means of determining the molecular weights of dissolved substances, since the mols per 1,000 grams of solvent is given by equation (7) from the boiling point elevation, and the grams of solute per 1,000 grams of solvent is known from analysis.

In equation (6) above the temperature coefficient of vapor pressure of the solvent, dp_o/dT, was used to determine the elevation of the boiling point, and the values in Table 53 were calculated from the slope of this curve. It will be recalled that the Clausius-Clapeyron equation expresses this change of vapor pressure in terms of the molal latent heat of evaporation. By substituting $dp_0/dT = p_oL/RT_o^2$ in equation (5) we have

$$\frac{dp_0}{dT} = \frac{p_0L}{RT_0^2} = \frac{p_0x}{T - T_0}$$

and on solving for ΔT we have

$$\Delta T = \frac{RT_0^2}{L}x = kx, \quad \text{or} \quad \Delta T = BC. \tag{8}$$

For comparison, let us calculate a value of B for water from this

TABLE 53.—BOILING POINT CONSTANTS[1]

Substance	Boiling point at 760 mm.	dp / dT atmospheres per degree	Molal boiling point raising, B	Correction for each 100 mm. change in total pressure
Acetic acid	118.51	0.0308	3.28	0.008
Benzene	80.15	0.0309	2.58	0.024
Carbon disulfide	46.00	0.0325	2.40	0.020
Chloroform	60.19	0.0329	3.64	0.010
Carbon tetrachloride	76.50	0.0314	5.05	0.036
Ethyl alcohol	78.26	0.0379	1.24	0.010
Ethyl ether	34.42	0.0358	2.21	0.007
Ethyl acetate	77.13	0.0317	2.90	0.012
Hexane	68.59	0.0313	2.89	0.007
Methyl alcohol	64.67	0.0399	0.84	0.009
Methyl acetate	57.11	0.0345	2.20	0.009
Methyl propionate	79.59	0.0330	2.77	0.016
Octane–*n*	125.80	0.0284	4.37	0.005
Pentane–*n*	35.98	0.0354	2.13	0.012
Propyl alcohol	97.14	0.0365	1.71	0.012
Propyl acetate	101.68	0.0299	3.61	0.010
Stannic chloride	114.20	0.0263	10.32	0.100
Water	100.00	0.0358	0.518	0.007

The corrections in the last column are to be added to B for every 100 mm. increase in the barometric pressure over 760 mm., and to be subtracted for every 100 mm. below 760 mm. For example the molal elevation for stannic chloride at a pressure of 700 mm. would be 10.26°.

equation, where B is the boiling point elevation for a molal solution. The heat of evaporation of water is 538 cal. per gram, or 9700 cal. per mol, whence

$$\Delta T = \frac{1.99 \times (373)^2}{9700} \times \frac{1}{1 + 55.5} = 0.508^\circ$$

when $C = 1.$

The agreement is about what may be expected in calculations involving the approximate equation $dp/dT = p_0L/RT^2$. When data for the molal heat of evaporation are not at hand, approximate values suitable for use in equation (8) may be calculated from Trouton's rule, or its modifications. Conversely, the elevation of the boiling point may serve to determine the heat of evaporation, provided deviations of 2 or 3 per cent are not objectionable.

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[1] Rosanoff and Dunphy, *J. Am. Chem. Soc.*, **36**, 1,415 (1914).

Fractional Distillation.—In the paragraphs just given, it has been assumed that the dissolved substance was not volatile. For the liquid mixtures mentioned earlier, each component has an appreciable vapor pressure, and the total vapor pressure may be greater or less than that of one of the components. For example, addition of acetone to toluene lowers the boiling point, for the partial pressure of acetone from such a solution is greater than the decrease in toluene pressure produced by adding a solute. If the total pressure is higher than the vapor pressure of pure toluene at the same temperature, the solution will exert a pressure of 1 atmosphere at a temperature lower than toluene boils, and will therefore have a lower boiling point. Distillation is ordinarily carried out at a constant pressure of 1 atmosphere, and fractions of distillate passing over at different temperatures are collected. The total vapor pressure is constant, and the mol fraction of each substance in the distillate passing off from any liquid mixture is equal to its mol fraction in the vapor at equilibrium with this solution; these mol fractions in the vapor being a measure of the partial vapor pressures from solution. The boiling points of mixtures of acetone and toluene are shown in Table 54, together with the partial pressure of each substance in the vapor in equilibrium with these solutions. For example a

TABLE 54.—VAPOR PRESSURES OF TOLUENE-ACETONE MIXTURES

Mol fraction acetone in solution	Boiling point of solution	Partial pressure of acetone	Partial pressure of toluene	Mol fraction of acetone in vapor
0.00	109.4	0	760	.....
0.108	93.5	341	419	0.449
0.187	85.0	484	276	0.636
0.383	72.8	616	144	0.811
0.572	67.0	671	89	0.883
0.686	64.0	696	64	0.916
0.790	61.2	715	45	0.941
0.871	59.5	732	28	0.964
0.938	58.0	746	14	0.981
1.000	56.5	760	...	1.000

Rosanoff, Bacon and White, *J. Am. Chem. Soc.*, **36**, 1,803 (1914).

mixture containing 68.6 mol per cent of acetone boils at 64°, that is, exerts a total vapor pressure of 760 mm. of mercury at this temperature; of which total pressure 696 mm. is due to acetone and 64 mm. to toluene. Since partial pressures are proportional to mol fractions in a gaseous mixture, the mol fraction of acetone in the vapor above this solution is 696/760 or 0.916, that of toluene is 64/760 or 0.084; and these are the mol fractions in the first portion of distillate passing over, since the distillate is formed upon condensation of this vapor.

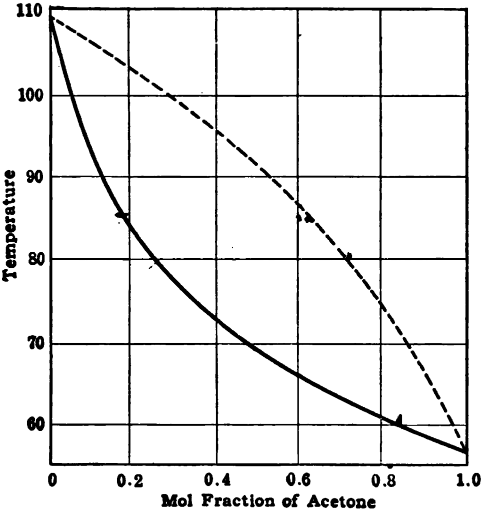

FIG. 24.—Boiling-point curve for mixtures of acetone and toluene.

In Fig. 24 the boiling points of the mixtures are plotted against mol fractions in the liquid, shown by a solid line; and the composition of the vapor in equilibrium with each solution is shown as a dotted line. Thus a solution of 25 mol per cent acetone boils at 80°, giving a first distillate which contains about 70 mol per cent of acetone. If the boiling is continued until 85° is reached, the last portion of distillate passing over has a composition of 64 mol per cent acetone, and the composition of the residual liquid is 19. mol per cent acetone. The composition of the total distillate is intermediate between 70 mol per cent and 64 mol per cent. Reference to the solid line of Fig. 24 shows that this distillate (assuming it 67 mol per cent acetone) would boil at about 64° and yield upon re-distillation a first distillate containing nearly 90 mol per cent of acetone. By repeating these fractionations a mixture richer in acetone is obtained as a distillate each time, and by combining the residues and distilling out a new portion, it is possible to resolve such a mixture into its components after a number of repetitions of this process. This is true of mixtures when the boiling points of all solutions are between those of the components, provided these components do not have boiling points too close to each other.

Mixtures with a Minimum Boiling Point.—Certain pairs of liquids form mixtures which boil lower than either of the constituents; such mixtures cannot be separated by distillation into the two pure components, but only into one pure liquid and a mixture having the lowest boiling point. For example, acetone and carbon bisulfide form a solution with a higher vapor pressure than either component (page 123); this solution will therefore boil at a lower temperature than either pure component.

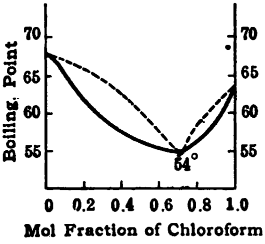

FIG. 25.

Similarly, methyl alcohol (boiling point 66°) and chloroform (boiling point 62°) form a mixture boiling at 54°, which mixture contains about two mols of chloroform for one of alcohol. The boiling point curve is shown by a solid line in Fig. 25 and the composition of distillate passing off at each boiling temperature is shown by the dotted line. A mixture of one mol of each substance boils at about 55°, yielding as a first distillate a mixture in which the mol fraction of chloroform is about 0.60. Complete fractionation of this mixture would yield pure methyl alcohol as a final residue, and the minimum boiling mixture as a final distillate. Any mixture containing over 66 mol per cent of chloroform may be fractionated into pure chloroform as a residue and the minimum boiling mixture as a final distillate. To each portion of the diagram of Fig. 25 may be applied the reasoning considered in connection with Fig. 24, where there was no minimum point. Ethyl alcohol and water are another pair of liquids forming a minimum boiling mixture, the 96 per cent alcohol of commerce. Certain other liquids form maximum boiling mixtures; they may be separated by fractionation into a distillate which is one pure component, and the maximum boiling mixture as a final residue; but not into the two pure components.

It frequently happens that maximum points or minimum points occur at percentage compositions which correspond to a simple molecular ratio of the two components. This is not very good evidence that a compound is formed however. For example, constant boiling hydrochloric acid has a composition closely approximating $HCl.8H_2O$ when distilled under a pressure of 1 atmosphere; a weaker acid solution expels more water than hydrogen chloride and becomes stronger; a more concentrated acid loses hydrogen chloride faster than it loses water, and becomes weaker in acid until this constant boiling composition is reached. A constant boiling acid solution of somewhat different composition is obtained when the distillation is carried out under reduced pressure or increased pressure, so that the existence of a loose chemical compound in solution must be established by some other means than a maximum point in the boiling temperature curve. Minimum points are possibly an indication of loose chemical combination between the constituents of a mixture, but in the lack of other and better evidence it is probably unsafe to assume that such compounds exist.

Distillation with Steam.—In all of the discussion of distillation given above, it has been assumed that there was only one liquid phase present. There is another type of distillation involving two phases, that is, two liquids which do not dissolve in one another. In this case each liquid exerts its own vapor pressure independently of the other liquid, and since the liquids are mutually insoluble, neither lowers the vapor pressure of the other by decreasing its mol fraction. When the total vapor pressure reaches that of the atmosphere, distillation takes place from both phases, and the mol fraction of each substance in the vapor passing over is proportional to its vapor pressure at the temperature of the distillation.

Consider for example a mixture of water and turpentine, under a total external pressure of 1 atmosphere. When the temperature is 90° the vapor pressure of water is 526 mm. of mercury, and that of turpentine is 91 mm. At 100° the vapor pressures are 760 mm. and 131 mm. The total pressures at each temperature are the sums of the two vapor pressures, since each liquid is substantially insoluble in the other; therefore the total pressure is 617 at 90° and 891 at 100°. Then at 90° the total pressure is below that necessary for boiling the mixture, and 100° it is considerably above the necessary temperature. At 95° the vapor pressures for the two pure substances are 634 and 110, total 744. It is clear that the mixture will boil slightly above this temperature.

The mol fraction of each substance in the vapor is proportional to its partial pressure, and the mol fraction of each substance in the distillate is the same as that in the vapor. Since the partial pressure of turpentine at 95° is about 0.15 atmosphere, and that of water is 0.85 atmosphere; under a total pressure of 1 atmosphere, these are the mol fractions of the two substances in the distillate. Then there will be 0.15 mols of turpentine for 0.85 mols of water, or 57 per cent of turpentine by weight. It should be noted that this process has effected the distillation of turpentine at about 95°, which is about 70° below its boiling point when distilled alone. Steam distillation is often resorted to in organic preparations when a substance decomposes at temperatures near its normal boiling point.

A distillation with steam can also be carried out for liquids which are mutually soluble to a small extent, such as water and aniline; but the temperature at which such a distillation will take place cannot be computed from vapor pressure data for the pure substances. In general, when the two liquids concerned are mutually soluble to a slight extent, the temperature of distillation is higher than if they were completely insoluble, but below the boiling point of either pure substance. Solid insoluble substances may be sublimed with steam also, since the current of steam serves to carry away saturated vapor as fast as it is formed, and the solid substance separates out when the vapor is cooled. When it is desired to distil or sublime substances of very small vapor pressures, superheated steam is often employed.

Freezing Point of Solutions.—The freezing point of a solution may be defined as the temperature at which the solution exists in equilibrium with the solid solvent; it is the temperature at which the solid solvent would begin to separate if the solution were cooled slowly. The addition of a solute will lower the vapor pressure of a solvent in accordance with Raoult's law, but will leave the vapor pressure of ice (in which the solute does not dissolve) unchanged. Thus the solution and ice will no longer be in equilibrium (have the same vapor pressure) at the freezing point of pure solvent. The sublimation pressure of ice decreases more rapidly as the temperature falls than does the vapor pressure of the solution, which changes at almost the same rate as the vapor pressure of pure solvent. Hence by lowering the temperature we may bring the solution and pure solid solvent to the same vapor pressure, that is, to equilibrium.

Let *ah* in Fig. 26 represent the vapor pressure of pure liquid solvent, *dbg* that of a solution in which the mol fraction of dissolved substance is x, and let *adm* represent the vapor pressure of ice. At *d* the vapor pressure lines for ice and the solution intersect; this is therefore the freezing point of the solution. It is desired to find the relation between *ab*, the vapor pressure lowering (connected with the mol fraction through Raoult's law) and *dc*, the lowering of the freezing point produced by the dissolved substance.

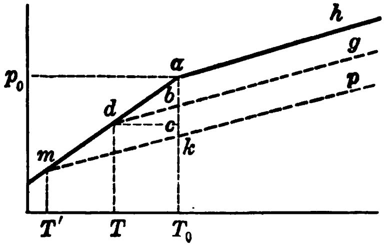

FIG. 26.

In the figure *ab* is *ac* − *bc*, and the relation *ab*/*dc* is (*ac*/*dc*) − (*bc*/*dc*). Now *ac*/*dc* is the slope of the line showing the change of the vapor pressure of ice with the temperature and *bc*/*dc* is the slope of the vapor pressure curve for water. As in the previous derivation, we may calculate *bc*/*dc* from the approximate form of the Clausius-Clapeyron equation. This equation may also be applied to the change of the vapor pressure of a solid, using L_s as the molal heat of *sublimation* of the solid, and as the volume increase the difference in volume between the saturated vapor and the solid forming it. Expressed as equations, these two slopes are

$$\frac{ac}{dc} = \frac{dp_i}{dT} = \frac{p_o L_s}{RT^2} \quad \text{and} \quad \frac{bc}{dc} = \frac{dp_o}{dT} = \frac{p_o L_v}{RT^2}$$

where RT/p_o is the volume of a mol of vapor. Upon subtracting one of these equations from the other, and noting that ab/dc is $(p_o - p)/(T_o - T)$, from the figure, we have

$$\frac{ac - bc}{dc} = \frac{ab}{dc} = \frac{[L_s - L_v]\,p_o}{RT^2} = \frac{p_o - p}{T_o - T}$$

Further, put for $(p_o - p)$ its equivalent $p_o x$ from Raoult's law, and for the difference between the heats of sublimation and evaporation, substitute its equal, the molal heat of fusion, L_f, and the equation becomes

$$\Delta T = T_o - T = \frac{RT^2}{L_f}x = F'x \qquad (10)$$

which is the desired equation. From it may be calculated the mol fraction of a solute in a solution provided its freezing point has been determined; or the freezing point may be calculated if the mol fraction of solute is known.

It will be seen from the figure that the triangles *abd* and *akm* are similar, and that *mkp* is the vapor pressure of a solution containing a larger mol fraction of dissolved substance in the solution. The vapor pressures of other solutions would be shown by lines parallel to these lines *dbg* and *mkp*. Hence the lowerings of vapor pressure (which are proportional to the mol fraction of the solute) are proportional to the lowerings of the freezing points.

This freezing point equation is valid only for dilute solutions; it should not be applied if the depression of the freezing point is more than 1 or 2 degrees.[1]

The freezing point equation may also be expressed in terms of the mols of solute per 1,000 grams of solvent, as was done for the boiling point equation, since in equation (10) RT^2/L_f is constant, and the mol fraction is proportional to the concentration in dilute solutions. This equation is

$$\Delta T_f = FC \qquad (12)$$

where the molal freezing point lowering F, corresponding to a solution of 1 mol of solute in 1,000 grams of solvent, is RT^2/L_f

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[1] The exact thermodynamic equation connecting the freezing point with the mol fraction is

$$\frac{d \ln (1 - x)}{dT} = \frac{L_f}{RT^2} \qquad (11)$$

When the depression of the freezing point is large, L_f must first be expressed as a function of the temperature before the equation is integrated. For dilute solutions the integral of this equation reduces to equation (10).

divided by the number of mols of solvent in 1,000 grams. Equation (12) states that the freezing point lowering in any solvent is proportional to the solute concentration, and that this lowering for a single mol of solute in 1,000 grams of solvent is $F°$. The numerical value of the proportionality constant F is different in different solvents. Values of it for the more common solvents are recorded in Table 55.

TABLE 55.—MOLAL FREEZING POINT CONSTANTS

Substance	Melting point	Molal lowering	Substance	Melting point	Molal lowering
Acetic acid	17	3.9	Bromine	−7.3	9.7
Formic acid	8	2.8	Stannic bromide	26.4	24.3
Water	0	1.855	Ethylene bromide	10	12.5
Benzol	5.5	5.12	Benzil	94	10.5
Naphthalene	80	6.8	Tribromphenol	95	20.4
Benzophenone	48	9.8	*p*-Xylol	16	4.3
Nitrobenzol	5.3	7.0	Aniline	− 6	5.9
Urethane	49	5.14	Acetamide	82	3.6
Carbon tetrachloride	−24	29.8	Chloroform	−61	4.68

Landolt and Bornstein's Tables, p. 793.

Molecular Weights.—Freezing point depressions offer the most convenient means of determining molecular weights in solution. They have two distinct advantages over boiling point elevations, in that the latter are considerably influenced by changing atmospheric pressure during the progress of a determination, while freezing point depressions are not affected; and the molal depressions of the freezing point are usually larger than the corresponding elevations of the boiling point for the same solvent. Also, at the low temperatures of freezing solutions there is less danger of losing solute by evaporation. The boiling point equation, it will be recalled, was derived for a solute which was not volatile, but nothing was said about the vapor pressure of the solute in the freezing point equation. The freezing point of an aqueous solution is the temperature at which the vapor pressure of ice is equal to the partial pressure of water vapor above the solution, and is independent of whether the solute has a vapor pressure or not.

By means of thermocouples it has been possible to measure very accurately the freezing points of quite dilute solutions. Usually the solution is made up somewhat stronger than needed, and poured over a quantity of crushed ice. The mixture is stirred until equilibrium is established, the freezing temperature is accurately determined, and a sample of the solution is withdrawn through a chilled filter and analyzed. This procedure is more accurate than that of chilling a solution of known concentration until ice begins to separate, for a correction must then be applied to allow for the ice which has separated. When a large quantity of ice is used, equilibrium is more readily and more certainly established, but it is often more difficult to determine the concentration of solution after freezing than to make it up of known strength. In Table 56 the freezing points of dilute solutions of mannite are shown; in Table 57 some illustrations of molecular weight determinations upon solutes in naphthalene are given.

Osmotic Pressure.—The molecules of a dissolved substance are free to move about in solution, and they are separated from one another by distances which (at least in dilute solutions) are large compared to the diameter of the molecules. This is strikingly similar to the condition of gas molecules; the chief difference being that in a solution there is another substance between the molecules, while in a gas the intermolecular space is void. To test out this similarity it would only be necessary to find a membrane which would allow free passage of the solvent and wholly stop the passage of the dissolved substance. A piston of this material could then be forced through pure solvent without encountering an opposing equilibrium pressure, but could not force solvent out of a solution and compress the dissolved substance into a smaller space without overcoming the pressure exerted by solute molecules. If our idea of this pressure is correct, the pressure exerted on this "semi-permeable" substance should be that which the substance would exert if it were a gas at the same temperature and in a volume equal to that of the solution; and the pressure should increase with the temperature in the same way that the pressure of a gas increases, or in proportion to the absolute temperature. For the calculation of this pressure, the existence of solvent can be ignored, while the dis-

Table 56.—Solutions of Mannite in Water[1]

Molal concentration	Freezing point depression	Lowering per mol of solute
0.006869	0.01274	1.853
0.01006	0.01846	1.847
0.01041	0.01930	1.855
0.02039	0.03790	1.859
0.02249	0.04171	1.854
0.05061	0.09460	1.868
0.06062	0.11265	1.858
0.09574	0.1790	1.870
0.1197	0.2225	1.858

Table 57.—Freezing Points of Naphthalene Solutions

Solute	Grams in 25 grams naphthalene	Lowering of freezing point	Molecular weight calculated from ΔT_f	Formula weight
Nitrobenzene	0.2540	0.57	122.9	123.1
	0.5080	1.13	123.9	
	0.7580	1.70	123.1	
Aniline	0.2407	0.72	92.1	93.1
	0.364	1.08	93.0	
	1.008	2.99	93.0	
Benzoic acid	0.361	0.83	120.0	122.1
	0.522	1.15	125.3	
	0.748	1.69	122.2	

Kozicki and Pilat, *Z. angew. Chem.*, **29**, (I), 423 (1916).

solved substance may be regarded as existing in the gaseous condition in the volume of the solution.[2]

The existence of such a pressure has been established by the use of membranes of copper ferrocyanide (among other substances) precipitated in the walls of a porous clay pot. Such a wall allows free passage of water, but retains sugar molecules. This pressure is called the "osmotic pressure" of a solution

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[1] Flügel and Roth, *Z. physik. Chem.*, **79**, 577 (1912).

[2] Jaeger, *Annalen der Physik*, **54**, 463 (1918).

(van't Hoff, 1886); it is due to the kinetic energy of the dissolved molecules just as the pressure of a gas is due to bombardment by its molecules; and its value is approximately equal to the pressure of a gas at the same concentration, provided this is not too large. The osmotic pressure of a mol of solute in 1,000 grams of water should be approximately that of a mol of gas confined in a liter, that is, about 25 atmospheres at room temperature. Just as the simple gas law $pv = nRT$ fails to express accurately the behavior of a gas under a pressure of 25 atmospheres, the osmotic pressure as measured is not exactly equal to the corresponding gas pressure. Osmotic pressure data has so far been taken for the most part with substances having quite complex molecules, owing to the difficulty of preparing membranes impermeable to the smaller molecules; and the deviations from the ideal gas law are always greater for complex molecules than for simple ones, hence this deviation is not surprising.

In spite of the experimental difficulties in connection with the work, Morse[1] and his co-workers have prepared membranes of satisfactory impermeability to sugar, glucose and mannite, by precipitating copper ferrocyanide or nickel ferrocyanide within the pores of clay vessels. After experiments extending over many years they were able to make these membranes of a quality suited to exact experimental work, and by means of them to measure accurately the osmotic pressures of several solutions over a range of temperature and concentration. The tables below have been taken from the final report of this work. Under

TABLE 58.—OSMOTIC PRESSURES OF MANNITE SOLUTIONS, IN ATMOSPHERES

Molal concentration	10°		20°		30°		40°	
	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio
0.1	2.314	1.002	2.395	1.002	2.467	0.999	2.557	0.998
0.2	4.609	0.998	4.781	1.000	4.943	1.000	5.107	1.000
0.3	6.940	1.002	7.181	1.001	7.430	1.002	7.664	1.001
0.4	9.209	0.997	9.570	1.001	9.881	0.999	10.216	1.000
0.5	11.613	1.006	11.960	1.001	12.345	0.998	12.804	1.003
0.6	......	.....	......	.....	......	.....	15.315	1.000

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[1] *Publ. Carnegie Inst.*, **198**, (1914).

TABLE 59.—OSMOTIC PRESSURES OF SUGAR SOLUTIONS, IN ATMOSPHERES

Molal concentration	0°		20°		40°		60°		Average ratio
	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	
0.1	2.462	1.106	2.590	1.130	2.560	0.998	2.717	1.000	1.06
0.2	4.723	1.065	5.064	1.060	5.163	1.012	5.438	1.001	1.03
0.4	9.443	1.060	10.137	1.060	10.599	1.037	10.866	1.000	1.04
0.6	14.381	1.077	15.388	1.071	16.146	1.053	16.535	1.015	1.05
0.8	19.476	1.091	20.905	1.093	21.806	1.068	22.327	1.025	1.07
1.0	24.826	1.130	26.638	1.130	27.701	1.085	28.367	1.045	1.10

the columns headed "Ratio" are given the ratios of the actual osmotic pressures measured to the calculated gas pressure. As the solutions were quite concentrated, a correction for the volume of the molecules was made by calculating the gas pressures at the volume of the solvent in the solution.

It will be seen that the osmotic pressures of sugar solutions are uniformly higher than the calculated gas pressures, but this is not strange in view of the complexity of the molecules. Gaseous substances with large molecules deviate considerably from the laws of ideal gases, and it is not in the least remarkable that dissolved substances do the same. Osmotic pressure determinations on simple dissolved molecules are very much needed, but the problem of finding a suitable membrane is greatly increased when smaller molecules are concerned. The results given show beyond question that there is a similarity between the behavior of a dissolved substance and that of a gaseous substance. In correspondence with the fundamental law of ideal gases, we may write

$$\pi = \frac{NRT}{v} \quad \text{or} \quad \pi = CRT \tag{13}$$

as an expression of the change of osmotic pressure π with the volume and temperature of the solution. The value of R in this equation is the same as that in the gas equation. If osmotic pressure is measured in atmospheres, the volume of solvent in liters, N is the mols of solute, and N/v is the molal concentration C, R is 0.082 liter-atmospheres, just as in the gas equation.

This equation $\pi = CRT$ can also be used to determine molecular weights in solution from measured osmotic pressures. If

m grams of solute having a molecular weight M are present in v liters of solvent,

$$\pi = \frac{mRT}{Mv}$$

and M is readily calculated. Osmotic pressure measurements are so difficult, from an experimental point of view, that molecular weights are seldom so determined. Boiling point elevations or freezing point depressions lead to the same molecular weights, and are far more easily carried out in the laboratory.

There is an equation connecting the osmotic pressure of a solution with its vapor pressure, which is quite accurate up to very high concentrations, if measured vapor pressures are used. This equation is

$$\pi = \frac{RT}{v_m} \ln \frac{p_o}{p} \tag{14}$$

where v_m is the volume of one mol of solvent, p_o is the vapor pressure of pure solvent and p the vapor pressure of solvent from the solution. For dilute solutions this equation reduces to equation (13) above when the vapor pressures are in agreement with those calculated from Raoult's law. For concentrated solutions p must be measured experimentally.

When osmotic pressures of strong solutions are calculated from equation (13), they do not agree with the results of experiment, and the deviations are serious. They are doubtless due in part to combination of solute and solvent (hydration), and to molecular association of the solvent. These same factors would lead to lower vapor pressures than those demanded by Raoult's law. But if the measured vapor pressure is substituted in equation (14), a calculated osmotic pressure in substantial agreement with the experimental one is obtained. This is illustrated in Table 60, where it will be seen that equation (14) represents the experimental data satisfactorily.

A symposium on osmotic pressure, presenting various points of view of prominent investigators, will be found in the *Transactions of the Faraday Society*, **13**, 119–189 (1917). Reference should also be made to the Monograph on Osmotic Pressure by Alexander Findlay (1913), where additional information will be found.

TABLE 60.—CANE SUGAR SOLUTIONS AT 30°

Molal concentration	Measured osmotic pressure[1] (atmospheres)	Calculated osmotic pressures			
		Equation (13)	Per cent error	Equation[2] (14)	Per cent error
0.10	2.47	2.47	0	2.47	0.0
1.00	27.22	24.72	9	27.0	1.0
2.00	58.37	49.40	15	58.4	0.0
3.00	95.16	74.20	23	96.2	0.0
4.00	138.96	98.90	29	138.3	0.5
5.00	187.3	123.60	33	182.5	2.5
6.00	232.3	148.30	36	230.9	0.6

Questions

1. The vapor pressure of acetic acid at 50° is 55 mm., that of benzol is 267 mm. Calculate the partial pressure of each from a solution in which the mol fraction of the acid is 0.30, and calculate the total vapor pressure. The measured total pressure is 236 mm. Calculate the per cent deviation.

2. The vapor pressure of CCl_4 at 50° is 308 mm., that of benzol is 267 mm. Calculate the total vapor pressure of a solution of one mol of CCl_4 in three mols of benzol. The observed pressure is 185 mm. What is the per cent error in the calculated pressure?

3. Steam is passed through a mixture of nitrobenzene and water, which are *not soluble in one another*, and the distillate is caught in a graduate. When the total volume of distillate is 100 c.c. the nitrobenzene layer is 13 c.c. What is the partial pressure of each substance in the vapor in the distilling flask, if the total pressure is 1 atmosphere? What is the temperature of the distillation? The vapor pressure of water changes 27 mm. per degree; the density of nitrobenzene is 1.20.

4. At 18° a liter of water dissolves a liter of CO_2 when the pressure of CO_2 is 1 atmosphere. Calculate the molal concentration in a solution over which the partial pressure of CO_2 is 150 mm.

5. From the data of Table 29 calculate the molal boiling point constants for ether and for ethyl alcohol, and compare them with those of Table 53.

6. Calculate the latent heat of evaporation of stannic chloride from its boiling point constant.

7. Carbon disulfide boils at 46°, its latent heat is 146 cal. per gram. Calculate its boiling point constant. A solution of 25 grams of sulfur in 1,000 grams of CS_2 boils at 46.24°. Calculate the molecular weight of dissolved sulfur.

8. A solution of 3.17 grams of anthracene (mol weight 178) in 100 grams of benzene boils 0.50° higher than pure benzene. Calculate the latent heat of evaporation of benzene.

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[1] Fraser and Myrick, *J. Am. Chem. Soc.*, **38**, 1,907 (1916).

[2] Vapor pressures from Berkley, *Phil. Trans. Roy. Soc. London*, **218**, 295 (1919).

9. Benzene, C_6H_6, freezes at 5.42° and boils at 80°. Its heat of vaporization at the boiling point is 95.46 cal. per gram. A solution of 12.8 grams of naphthalene, $C_{10}H_8$ in 1,000 grams of benzene freezes at 4.918°. (*a*) At what temperature will this solution boil? (*b*) What will be the vapor pressure of benzene above this solution at 80°? How many calories are absorbed during the melting of a gram of benzene? What is the vapor pressure of pure benzene at 70°?

10. The vapor pressure of CH_3OH at its boiling point, 66°, changes 17.7 mm. per degree. Calculate the boiling point of a solution containing 2 grams of a non-volatile solute of mol weight 65 in 96 grams of alcohol.

11. Naphthalene melts at 80.05°, and a solution containing 9.21 per cent by weight of phthalic anhydride is in equilibrium with solid naphthalene at 75.1°. Calculate the molecular weight of phthalic anhydride.

12. Phthalic anhydride melts at 130.84°, and a solution containing 8.30 per cent by weight of naphthalene is in equilibrium with solid anhydride at 124.8°. (*a*) Given the molecular weights of both substances, calculate the latent heat of fusion of a mol of phthalic anhydride, and the molal freezing point depression. (*b*) Calculate the freezing point of a solution of 4 mols of phthalic anhydride and 1 mol of naphthalene. The observed freezing point of this solution is 118°.

13. A solution containing 29 per cent by weight of phthalic anhydride is in equilibrium with both solid naphthalene and solid phthalic anhydride. Calculate the freezing point from equation (10), first considering naphthalene as the solvent, then phthalic anhydride as the solvent. The observed freezing point is 65°. Calculate the percentage error in applying the freezing point for dilute solutions to a solution which is obviously not dilute.

14. A solution of 0.60 grams of acetic acid in 50 grams of water freezes at −0.375°. Calculate the molecular weight of a solute 68 grams of which in 1,000 grams of water lowers the freezing point 0.469°.

15. The vapor pressure of a solution of 2.38 mols of sugar in 1,000 grams of water at 30° is 94.88 per cent that of pure water. Calculate the osmotic pressure of this solution from the vapor pressure. Calculate also its osmotic pressure assuming that it behaves as an ideal gas at this concentration. The measured osmotic pressure is 73 atmospheres.

16. Make the same calculations as in the previous problem for a solution of 5.35 mols of sugar per 1,000 grams of water, where the vapor pressure is lowered 13.24 per cent, and calculate the percentage deviation from the measured osmotic pressure, 128.6 atmospheres at 30°.

CHAPTER VI

SOLUTIONS OF IONIZED SUBSTANCES

There is a class of solutions to which the laws developed in the previous chapter do not apply without some alteration. This includes solutions of practically all inorganic substances in water, in anhydrous formic acid, in liquid ammonia, and some other solvents. The vapor pressure, freezing point, boiling point and osmotic pressure of these solutions, when used to calculate the mol fractions of solutes, lead to numbers inconsistent with the smallest possible molecular weights. These facts, and the further fact that such solutions conduct electricity, have led to the theory that solutes are frequently dissociated into charged parts of molecules in solution. The essential features of this commonly accepted theory are as follows.

1. The molecules of certain substances spontaneously dissociate upon solution in water (and some other solvents) into two or more portions, bearing equal charges of electricity of opposite sign, and called ions.

2. The dissociation is not complete, but varies from a slight fraction in some cases (acetic acid and ammonium hydroxide) to a very large fraction in other cases (salts, strong acids and bases). In all solutions the fraction of dissolved substance dissociated into ions increases with decreasing concentration, and approaches unity (complete dissociation) as the concentration approaches zero.

3. The conduction of electricity by these solutions is due to the motion of ions through the solution. Positively charged ions move toward the negative pole and there give up their charges, always with an accompanying chemical reaction; negatively charged particles move toward the positive pole and there give up their charges, at the same time causing a chemical reaction. Positive ions are called *cations*, the electrode toward which they move is the *cathode*, the reaction taking place there is the cathode reaction. Negative ions are *anions*, the electrode toward which

they move is the *anode*, and these ions there produce the anode reaction. The cathode reaction always consists in reduction, one species of which is deposition of metal upon the cathode; and the anode reaction is always oxidation, which may be solution of the anode, deposition of the material of the anion, or oxidation of a dissolved substance, depending upon the material composing the anode. Thus in the electrolysis of salt brine, chlorine is evolved at the anode if this consists of a carbon rod, zinc chloride is formed in solution if it consists of zinc, insoluble silver chloride forms as a film over the electrode when it is made of silver, and if a platinum electrode surrounded by ferrous chloride is used as an anode, ferric chloride is formed in solution. At the negative pole (the cathode) hydrogen is evolved and sodium hydroxide forms in solution with an iron or other metal electrode, but if silver chloride is spread upon the cathode, it is reduced to metallic silver, no gas is evolved and no hydroxide is formed. These electrochemical reactions are further considered under "Faraday's Law."

4. Ions have charges which are exact whole multiples of a definite unit charge, that of the electron. No atom can have a charge less than this unit without losing all of its charge, no ion ever has a fractional part more than a unit charge. Each negative ion in a chloride solution bears exactly the charge of an electron; nitrate ions, iodide ions, acetate ions, and all others which constitute a univalent group bear this same charge. Corresponding positive ions have charges of the same size but opposite sign, and always in whole multiples of the unit charge; hydrogen, sodium, potassium, ammonium and other groups bear a single charge, copper and magnesium a double charge, etc. This unit charge is 1.591×10^{-20} absolute electromagnetic units, or 1.591×10^{-19} coulombs; such a quantity of positive electricity is found upon each atom of sodium, and such a quantity of negative electricity upon each atom of chlorine in a solution of sodium chloride.

5. Ions behave like molecules of solute as regards the properties of solution governed by the mol fraction (vapor pressure, freezing point, boiling point, osmotic pressure). Thus a solution containing a formula weight of hydrogen chloride begins to deposit ice at −3.2°, indicating that about three quarters of the

solute added has dissociated into ions, producing one positive ion and one negative ion (therefore two particles of solute) for each molecule ionized. Each of these particles exerts the same effect upon the freezing point as a whole molecule.

Types of Electrolytes.—Ionizing substances are divided into classes according to their products upon ionization. Simple binary (or uni-univalent) electrolytes are those such as hydrochloric acid, sodium nitrate and potassium acetate, which yield a single positive ion bearing a unit charge, and a single negative ion bearing a unit charge for each molecule ionized. Substances of this type exhibit the simplest phenomena in ionization, and they have been more studied than salts of other types. Another simple type of ionization is that exhibited by copper sulfate and other salts similar to it; each ion bears two units of electricity upon it, but a molecule forms only two ions. These salts are much less ionized at the same *equivalent* concentration. Thus a solution 0.1 formal in sodium nitrate is about 86 per cent ionized; a solution 0.05 formal in copper sulfate (equivalent to 0.10 formal uni-univalent salt) is only about 40 per cent ionized. In 0.1 formal copper sulfate, which should be compared with 0.1 normal sodium chloride so far as freezing points are concerned, the fractional ionization is 0.35.

The remaining types of electrolytes are more puzzling in their behavior, on account of the possibility (not to say probability) of ionization in two different ways. A part of sulfuric acid[1] ionizes to produce hydrogen ions and sulfate ions according to the reaction $H_2SO_4 = 2H^+ + SO_4^{--}$; and at the same time another portion of it ionizes to produce hydrosulfate ions, $H_2SO_4 = H^+ + HSO_4^-$. Owing to the uncertainty which exists regarding the fractional ionization according to each type, the treatment of such electrolytes is more difficult than is that of simpler types of salts. In a few special cases such as that of sulfuric acid, there are independent methods of determining the total concentration of some particular ionic species, so that the fractional ionization values may be computed; but for the majority of these substances, no method of determining the intermediate ion concentration is known. It is customary to treat such salts as if there were no intermediate ions at all, and to assume that the ionization is all of the simple type, but this procedure is unsatisfactory in the extreme,[1] except when the solutions are below 0.01 normal.

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[1] Noyes and Stewart, *J. Am. Chem. Soc.*, **32**, 1,133 (1910).

Extent of Ionization.—One of the chief problems of physical chemistry has been a determination of the extent to which various substances ionize in solution. The products of such ionization are written with a positive sign attached to indicate one unit of positive electricity per atom or group, and with a negative sign attached to indicate the opposite charge; two positive signs indicating two unit charges per group. Thus the products of ionization of sodium chloride are written Na^+ and Cl^-, and the ionization of sulfuric acid is written

$$H_2SO_4 = H^+ + H^+ + SO_4^{--}$$

to indicate that a molecule of it forms two hydrogen ions and one doubly charged negative ion, sulfate ion. Let γ be the fraction of a simple salt ionized in a solution containing C formula weights per liter of solution.[2] Consider first a solute which gives only two ions from each molecule, one positive and one negative ion. Then the concentration of positive ion will be $C\gamma$, that of the negative ion will also be $C\gamma$, and the concentration of the non-ionized molecules will be the remainder, or $C(1 - \gamma)$. A charged particle or ion lowers the freezing point of a solution to the same extent as an un-charged molecule, since it has a separate existence in the solution, is free to move about in the solution just like a molecule, and differs only in having an electric charge upon it. The concentration of dissolved substance is the sum of the concentration of each molecular species, or $C\gamma + C\gamma + C(1 - \gamma) = C(1 + \gamma)$. This means that each formula weight of solute added produces $(1 + \gamma)$ mols of solute. The freezing point of a water solution therefore will not be $1.86\ C$, but $(1 + \gamma)$ times this quantity. Conversely the observed freezing point may be divided by 1.86 C to give a value of $(1 + \gamma)$ from which the extent of the ionization may be calculated. In Table 61 are shown the freezing points of some dilute solutions, together with the degrees of ionization as calculated from them.

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[1] See McBain, *J. Am. Chem. Soc.*, **34**, 1,134 (1912); Harkins, *Ibidem*, **33**, 1,872 (1911).

[2] On account of the fact that the electrical properties of a solution depend upon its total volume, not upon the mol fraction of solute, concentrations must be expressed in equivalents per liter of solution. In solutions which are not too concentrated this is essentially equal to equivalents per 1,000 grams of water; but in concentrated solutions the difference is several per cent. A solution containing one equivalent per liter is called a normal solution, as in volumetric analysis.

TABLE 61.—FREEZING POINT LOWERINGS, MOLS OF SALT PER FORMULA WEIGHT AND CALCULATED DEGREES OF IONIZATION

Formal concentration	Freezing point lowering	Lowering per formula weight	Mols of solute per formula weight of salt	Degree of ionization as calculated from freezing point
		Potassium nitrate[1]		
0.002	0.00731	3.655	1.967	0.967
0.005	0.01819	3.638	1.958	0.958
0.010	0.03599	3.599	1.937	0.937
0.020	0.07088	3.544	1.908	0.908
0.050	0.17150	3.431	1.848	0.848
0.100	0.33140	3.314	1.787	0.787
		Potassium chloride[1]		
0.002	0.007316	3.658	1.969	0.969
0.005	0.01822	3.643	1.961	0.961
0.010	0.03609	3.609	1.943	0.943
0.020	0.07140	3.570	1.922	0.922
0.050	0.1752	3.505	1.888	0.888
0.100	0.3451	3.451	1.861	0.861
		Sodium bromate[2]		
0.001	0.003689	3.689	1.985	0.985
0.002	0.007365	3.683	1.980	0.980
0.005	0.01828	3.656	1.967	0.967
0.010	0.03607	3.607	1.940	0.940
0.020	0.07134	3.567	1.913	0.913
0.050	0.1742	3.485	1.875	0.875
0.100	0.3409	3.409	1.835	0.835

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[1] Adams, *J. Am. Chem. Soc.*, **37**, 495 (1915).

[2] Flugel and Roth, *Z. physik. Chemie*, **79**, 557 (1912).

Magnesium sulfate[1]

0.005	0.01588	3.175	1.708	0.708
0.010	0.0300	3.000	1.614	0.614
0.020	0.0565	2.825	1.520	0.520
0.050	0.1294	2.589	1.394	0.394
0.100	0.2420	2.420	1.303	0.303
0.200	0.4504	2.252	1.214	0.214
0.500	1.0180	2.036	1.099	0.099

Since the lowering of the freezing point and elevation of the boiling point are both due to a change in the vapor pressure of solvent on account of a decrease in its mol fraction, it will be seen that corresponding elevations of the boiling points of the solutions are to be expected. However, since the molal boiling point elevation for water is 0.518° and the molal freezing point lowering is 1.86°, it will be clear that the latter serves as a more accurate measure of the extent of ionization. It so happens that ionization varies but little with the temperature (there is a slight decrease at higher temperatures), and hence the fraction γ is substantially the same at all temperatures, as shown by the two methods, for any given concentration.

An examination of all available data upon freezing points[2] of salts in aqueous solution shows that salts of the same type ionize to about the same extent at a given concentration. Thus for salts of the KCl type (giving one positive ion and one negative ion) the maximum and minimum ionizations at various concentrations were as follows:

TABLE 62.—IONIZATION AT VARIOUS CONCENTRATIONS

Concentration	0.005	0.01	0.02	0.05	0.1	0.2	0.5
Highest ionization.....	0.963	0.943	0.943	0.892	0.875	0.850	0.824
Lowest ionization......	0.944	0.928	0.907	0.878	0.856	0.829	0.778
Average............	0.952	0.937	0.925	0.887	0.864	0.837	0.804

Salts of the type of sodium sulfate and barium chloride are less ionized at a given equivalent concentration (in the sense used in volumetric analysis); those of the copper sulfate type are still less ionized.

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[1] Hall and Harkins, *J. Am. Chem. Soc.*, **38**, 2,672 (1916).

[2] Noyes and Falk, *J. Am. Chem. Soc.*, **32**, 1,011 (1910).

Vapor Pressure Lowering for Ionized Substances.—In Table 63 are shown the vapor pressure lowerings for solutions of potassium chloride[1] together with the vapor pressure lowering for mannite solutions of the same concentration. Upon dividing the figures in the second column by those in the third, a value of $(1 + \gamma)$ is obtained, from which the fractional ionization may be obtained by subtracting 1. It will be seen that the ionization values so obtained are in substantial agreement with those based on freezing point determinations.

TABLE 63.—VAPOR PRESSURE OF POTASSIUM CHLORIDE SOLUTIONS AT 20° COMPARED WITH MANNITE SOLUTIONS

Formal concentration	$p_0 - p$ for KCl	$p^0 - p$ for mannite	Ionization value of KCl	
			from vapor pressure	from freezing point
0.05	0.0294	0.0156	0.885	0.885
0.10	0.0574	0.0311	0.846	0.861
0.20	0.1128	0.0622	0.814	0.833
0.30	0.1680	0.0934	0.799	.....
0.40	0.2225	0.1243	0.790	.....
0.50	0.2785	0.1555	0.790	0.800

Osmotic Pressures of Electrolytes.—On account of the relatively small size of the ions and their chemical action on the substances which serve as membranes in osmotic pressure determinations, few determinations of the osmotic pressure of ionized substances have been made, but these experiments[2] lead to about the same values of the fraction ionized as do freezing point and boiling point experiments.

It will be seen from Table 64 that the ratio of osmotic pressure to the calculated ideal gas pressure is much larger than for non-ionized solutes such as were discussed in the previous chapter. On account of hydration of lithium chloride, this ratio is not a good measure of the fractional ionization, but the high value of it shows again that there is considerable ionization taking place in these solutions.

[1] Lovelace, Fraser and Sease, *J. Am. Chem. Soc.*, **43**, 119 (1921).

[2] Morse, *Publ. Carnegie Inst.*, **198** (1914), page 217.

Table 64.—Osmotic Pressures of Lithium Chloride as 30°

Concentration of salt, mols per 1,000 grams of water	0.10	0.20	0.30	0.40	0.50
Observed osmotic pressures	4.317	8.976	13.768	18.772	24.162
Calculated gas pressure for undissociated salt	2.472	4.943	7.415	9.866	12.358
Ratio osmotic pressure to ideal gas pressure	1.746	1.816	1.857	1.955	1.992

Conduction of Electricity.—Solutions which have the properties discussed above also conduct electricity; those which do not show these deviations from the molal properties of solutions do not conduct. On account of this property of conducting electricity, the substances which ionize in solution are called electrolytes. There is one fundamental difference between the conduction of these solutions and that of the metals. Metallic conduction is not accompanied by the movement of matter, while *electrolytic conduction* is accompanied by the movement of matter, and by the separation at the electrodes of the ions of the solution, or of the products of their discharge. Thus when copper chloride solution is placed between two inert electrodes, copper is deposited upon the negative one and chlorine is evolved from the positive one. Decomposition of a dissolved substance into two portions which appear at different places is called *electrolysis;* metallic conductors through which electricity enters and leaves the solution are the *electrodes.* We shall consider three distinct steps in connection with the passage of electricity through solution, though it is understood that these three steps actually occur simultaneously. (*a*) There is a chemical reaction by which electricity passes from electrode to the solution; (*b*) there is a transfer of charged particles of matter through the solution in opposite directions (the motion of positive ions in one direction being equivalent to the motion of negatively charged ions in the opposite direction); and (*c*) another chemical reaction by which electricity passes from the solution to the second electrode and out of solution. These chemical changes will be considered first; then the mechanism and laws of conduction.

Faraday's Law.—Consider four solutions containing electrodes as follows: (*a*) sodium chloride solution, with a carbon anode and a platinum cathode; (*b*) sodium chloride solution, with a zinc anode and a silver chloride-coated cathode; (*c*) silver nitrate solution with a platinum anode and a platinum cathode; (*d*) copper sulfate with a platinum anode and platinum cathode, and let these four cells be connected in series so that the positive electrode of the second is connected to the negative of the first, and so on, as shown in Fig. 27. If a current of electricity is passed through these cells, the products of electrolysis will appear as deposits upon the electrodes, as gases evolved from solution, or as new solutes in solution near the electrodes, as follows: (*a*) chlorine is evolved from the carbon anode, hydrogen is evolved from the platinum cathode and sodium hydroxide is formed in the solution around it; (*b*) zinc chloride is formed in solution around the zinc anode, silver chloride is reduced to silver at the cathode and sodium chloride is formed around the electrode; (*c*) oxygen is evolved from the platinum anode, nitric acid forms around it, and silver is deposited upon the platinum cathode; (*d*) oxygen is evolved from the anode, sulfuric acid is formed in solution near it, and copper is deposited upon the cathode.

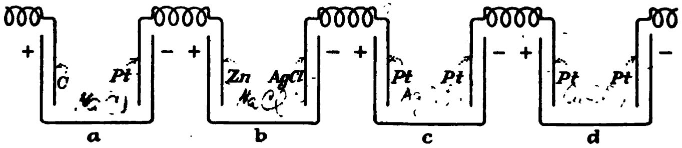

FIG. 27.

The solutions are not assumed to be of the same strength, or at the same temperature, or of the same resistance; the only condition imposed is that all of the electricity which passes through one cell must also pass through the others. A quantitative examination of the products of electrolysis will show that the sulfuric acid formed in *d* is just sufficient to neutralize the sodium hydroxide formed in *a*; that the chlorine evolved in *a* will convert all of the silver deposited in *c* into silver chloride; or all of the copper from *d* into copper chloride; that the silver formed from silver chloride in *b* is equal in weight to that deposited in *c*; the sodium hydroxide of *a* will precipitate all of the zinc chloride from *b* as zinc hydroxide; and that if this is ignited to zinc oxide, the oxide so formed is just sufficient to react with the sulfuric acid of *d*. In other words, the substances produced during electrolysis are equivalent to one another. Upon passing twice as much electricity through the solutions, twice as much of each product is formed; these two statements together constitute Faraday's law: The quantity of chemical action produced at *each electrode* by the passage of electricity is strictly proportional to the quantity of electricity, and dependent upon that alone; and in such electrolysis chemically equivalent quantities of substance are produced at the electrodes.

Faraday's law is absolutely exact under all conditions; no exceptions to it are known, and on it is based the definition of unit current. A current of one ampere is that current which will deposit in one second from a solution of silver nitrate, 0.0011180 grams of silver. This quantity of electricity is called an ampere-second or one coulomb. It is of interest to compute the quantity of electricity necessary to deposit one chemical equivalent, or one atomic weight of silver; since this is the quantity of electricity which will deposit one equivalent of any other substance from solution. The desired figure is $\frac{107.880}{0.0011180} =$ **96,500 coulombs.** This quantity of electricity is called **one faraday** of electricity, after the name of Faraday, the discoverer of the law. We may now state this important law again in the form: The passage of one faraday of electricity through a solution will liberate one chemical equivalent of some substance at *each electrode*. It is important to note that chemical action is required to pass electricity into a solution, and further action to pass it out again, so that one equivalent of electrolytic product is formed at *each* electrode.

Much experimental work has been done[1] on the electrolysis of silver nitrate solutions in connection with the definition of the international ampere, particularly by our own Bureau of Standards and the English National Physical Laboratory. An interesting confirmation of Faraday's law was obtained[1] by depositing silver in a standard instrument (called a coulometer), while in the same circuit iodine was liberated by the electrolysis of a solution of potassium iodide. The ratio of the weight of silver deposited to that of iodine liberated was 1 : 1.1762 as shown in Table 65.

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[1] *Bulletin Bureau of Standards*, **1**, 1 (1904); **9**, 494 (1912); **10**, 425; **11**, 220, 555 (1914); *Sci. Paper No.* **283** (1916); Richards, *Proc. Amer. Acad.*, **37**, 415 (1902); **44**, 91 (1908); *J. Am. Chem. Soc.*, **37**, 692 (1915); Smith, Mather and Lowry, *Res. Nat. Phys. Lab.*, **4**, 125.

TABLE 65.—DATA ILLUSTRATING FARADAY'S LAW

Weight of silver deposited	Weight of iodine deposited	Calculated coulombs		Difference in per cent	Milligrams of iodine per coulomb	Value of the faraday (I = 126.92)
		From silver coulometer	From potential and resistance			
4.10469	4.82862	3,671.45	3,671.53	0.0002	1.31518	96,504
4.09903	4.82224	3,666.39	3,666.55	0.0004	1.31526	96,498
4.10523	4.82851	3,671.94	3,671.84	0.0003	1.31498	96,518
4.10475	4.82860	3,671.51	3,671.61	0.0003	1.31515	96,506
4.10027	4.82247	3,667.50	3,667.65	0.0004	1.31492	96,523
4.10516	4.82844	3,671.88	3,671.82	0.0001	1.31498	96,519

Average value of the faraday: **96,515.**

The same ratio has been used by many investigators to determine the ratio of the atomic weights of these elements. An average of the ratios so obtained by very careful gravimetric work is 1 : 1.1763, which agrees with the electrochemical ratio 1 : 1.1762 within 1 part in ten thousand. Faraday's law is therefore an *exact* law of nature; it does not deviate in strong solutions like Raoult's law, it is exact at all temperatures,[2] and in all solvents.[3] In a mixture of dissolved substances, if several chemical actions occur at one electrode, the sum of the equivalents liberated in all the various reactions is exactly that required by Faraday's law. This law does not state what substance will deposit first from solution, or whether a mixture separates or not, but only that the products separating at two electrodes in the same circuit shall be chemically equivalent.[1]

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[1] Bates and Vinal, *J. Am. Chem. Soc.*, **36,** 916 (1914); *Bull. Bureau of Standards*, **10,** 425 (1914).

[2] Richards and Stull, *Proc. Amer. Acad.*, **38,** 409 (1902). Silver was deposited from an aqueous solution of silver nitrate at 20° and in the same circuit from silver nitrate dissolved in fused sodium nitrate and potassium nitrate at 250°. The weights of silver deposited agreed within 1 part in 20,000.

[3] Kahlenberg, *J. Phys. Chem.*, **4,** 349 (1900).

Chemical Reactions at The Electrodes.—It has been stated above that Faraday's law says nothing about which of several possible reactions will occur at any electrode, but governs only the total quantity of chemical action there produced. The *electrical potential* determines which reaction occurs, and the reaction which will occur with the smallest applied potential always takes place first. For instance in cell *a* of Fig. 27, hydrogen was evolved at the cathode, and no sodium was deposited. Reference to the electromotive series of elements in an inorganic chemistry text will show that sodium is near the top of the list, while hydrogen is well down in it. Quantitatively, the potential required to deposit sodium is nearly 3 volts higher than that required to discharge hydrogen ions. As some hydrogen ions are present from the slight ionization of water, these are therefore discharged, and the required potential for sodium is never reached. Similarly in *b*, the potential required to discharge chlorine at the zinc anode is 2 volts higher than that required for zinc to pass into solution. *The reaction requiring the lowest potential always takes place first.* There are of course hydrogen ions from water in the silver nitrate solution of *c*, but the potential required to discharge them is higher than that required for silver by about 0.8 volt; and the metal therefore deposits. In *a*, chlorine is evolved at the anode in place of oxygen from the hydroxide ions of water, because chlorine has a lower discharge potential than oxygen.

Measurement of Quantity of Electricity.—The number of ampere-seconds or coulombs of electricity passing through an electric circuit is best measured through an application of Faraday's law, by weighing the metal deposited on an electrode placed in the circuit. Silver is deposited from silver nitrate solution upon a weighed platinum dish when accurate results are desired, and when the quantity of electricity involved is not too large.

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[1] For other experiments confirming Faraday's law, see Fischer and Thiele, *Ztsch. anorgan. Chem.*, **67**, 302 (1910); Betts and Kern, *Electrician*, **54**, 16 (1904); Eisenreich, *Ztsch. physik. Chem.*, **76**, 643 (1910); Carhart, *Trans. Am. Electrochem. Soc.*, **9**, 375 (1906); Hulett and Vinal, *Bull. Bureau Standards*, **11**, 553 (1914); Smith, Mather and Lowry, *Phil. Trans. Roy. Soc. London*, **207**, 545 (1908); Rosa, Vinal and McDaniel, *Bull. Bureau Standards*, **9**, 209 (1913).

The standard instruments in which this is done are shown[1] in Figs. 28 and 29. It is necessary that the increase in weight be due *only* to the electric deposition of silver, and not to silver nitrate included in the crystals or to powdered silver from the disintegration of the anode, if accurate results are desired. To prevent inclusion of silver nitrate, the deposits are carefully washed with many portions of distilled water; it has been determined that inclusions of silver nitrate in a well-washed deposit[2] are not over 0.03 per cent, and they may be as low as 0.004 per cent.

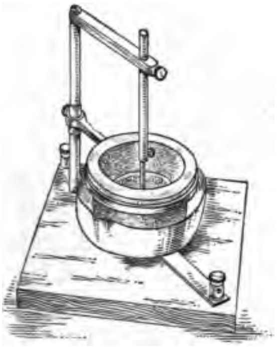

FIG. 28.—Porous cup type of silver coulometer, set up for use.

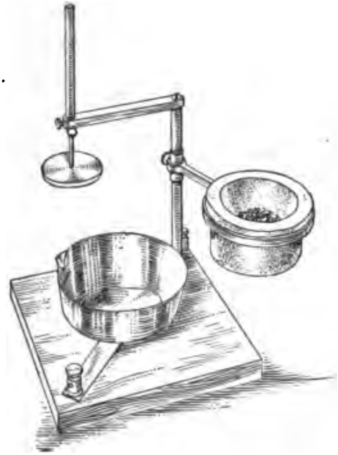

FIG. 29.—Parts of silver coulometer.

Unless precautions are taken to prevent the electrolyte around the anode from reaching the cathode, deposits are obtained which are too heavy, due to the formation of some unknown substance at the anode (possibly colloidal charged silver) which deposits and is not removed by washing. Porous cups or perforated glass shields are placed around the silver anode to avoid this disturbing factor. Exceptional care is used in securing pure silver nitrate for use in coulometers, as the presence of some other substance might lead to its inclusion in the weighed deposit. Such silver nitrate after very careful purification still gives high deposits if a filter paper is wrapped around the dissolving silver anode. This simple means of protecting the cathode from dust falling off the anode during its electrochemical disintegration must therefore be condemned when careful work is being done. Presumably the organic matter contained in even the best washed filter paper exerts a reducing action upon silver nitrate, forming colloidal silver which is deposited on the cathode, or at least forming something which leads to a greater quantity of silver deposit per faraday then does pure silver in the absence of filter paper. Errors due to filter paper protection of anodes are usually less than a tenth of 1 per cent, and when this accuracy is sufficient, filter paper is not objectionable. But for the accurate work of which a silver coulometer is capable, filter paper must not be used. Porous clay pots are suitable vessels for protecting the cathode, and they are not of too high resistance for convenient use.

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[1] *Bull. Bureau of Standards*, **1**, 3 (1904).

[2] Richards and Anderegg, *J. Am. Chem. Soc.*, **37**, 675 (1915).

When commercial quantities of electricity are involved, the use of silver is out of the question, and copper is usually deposited from copper sulfate for this purpose. Lead from solutions of lead silicofluoride may also be used, or the volume of hydrogen evolved from a negative electrode in acid solution may be measured. The commercial processes of copper refining and electroplating of one metal upon another are every-day confirmations of the law of electrolysis. It is the universal experience in such processes that the weight of metal deposited is strictly proportional to the quantity of electricity passed through the electro-plating cell when the current is not allowed to cause other reactions, such as the evolution of gas from the electrodes.

Resistance and Conductivity.—The familiar law of Ohm that the current flowing in a conductor, I, is equal to E, the applied electromotive force divided by R, the resistance of the conductor, applies also to solutions which conduct, the solutes of which are called electrolytes. This law, $I = \frac{E}{R}$, is often used in a form in which the resistance R is replaced by its reciprocal $\frac{1}{R}$, which is called the conductivity, and denoted by L'. Ohm's law is then

$$I = EL' \tag{1}$$

The specific resistance of a substance is the resistance of a centimeter cube of it, the reciprocal of this is the specific conductance, L. The conductivity of any substance increases with its cross section and decreases in proportion to its length. If the specific conductivity is L, the conductivity of a quantity of material in some other form than a centimeter cube is

$$L' = L\frac{q}{l} \tag{2}$$

where q is the cross section and l the length of the conductor. Conductivity is expressed in reciprocal ohms; thus if the resistance is 175 ohms, the conductivity is $1/175 = 0.005715$ reciprocal ohms.

It is often more convenient to consider another property of a solution, called its equivalent conductivity. Imagine two electrodes 1 cm. apart, parallel to each other, and of indefinite extent, between which is placed such a quantity of solution that there is an equivalent of electrolyte present. Thus if the solution is normal, the volume of solution required is a liter, the cross section of the conducting material is 1,000 sq. cm.; if it is tenth normal, 10 liters of solution are required, and the cross section of conducting material is 10,000 sq. cm. In the former case, this conductivity is called the equivalent conductivity of the normal solution, in the latter case the equivalent conductivity at tenth normal, etc. In general, when there is an equivalent of electrolyte between two electrodes 1 cm. apart, the conductivity is the *equivalent conductivity* of the salt in question. The relation between equivalent conductivity and specific conductivity is shown by equation (2), where q is one thousand times the number of liters containing an equivalent, hence it is $1{,}000/C$ if C represents the equivalent or normal concentration of the solution. In the example stated above, the equivalent conductivity of a normal solution would then be $1{,}000L$. If the solution is half normal, the volume containing it will be two liters, the cross section 2,000 square centimeters and the equivalent conductivity would be the new specific conductivity, $L_{0.5}$, multiplied by the new cross section. This equivalent conductivity is usually denoted by the Greek letter lambda with a subscript to indicate the concentration, thus $\Lambda_{0.5}$ for a half-normal solution. Then for any concentration the equivalent conductivity is obtained by multiplying the specific conductivity at that concentration by the cross section of the conductor, which is the volume of solution containing an equivalent. The general relation is

$$L = \frac{C\Lambda}{1{,}000}. \tag{3}$$

Equivalent Conductivity and Concentration.—The extent of ionization has been found (for example, from freezing point determinations) to increase as the concentration of a solution decreases. We should therefore expect the equivalent conductivity to increase as the concentration decreases, since there will be an increasing number of ions or conducting particles in the solution. The specific conductivity will at the same time decrease, since the small increase in ionization is more than off-set by the decreased quantity of salt per centimeter cube. When the solution has been diluted until ionization is complete, a limiting value of equivalent conductivity will be reached.

Suppose 10 c.c. of a normal solution of copper sulfate to be placed between two large copper plates 1 cm. apart, to which a potential of 1 volt is applied. As the conductivity is numerically equal to the current flowing when the applied potential is unity, the current will be numerically equal to one hundredth of the equivalent conductivity, since one hundredth of an equivalent is between the plates. If the temperature is 18°, $100\ I$, or the equivalent conductivity of copper sulfate at normal, is 25.7. Now pour 40 c.c. of water between the plates, and stir. The quantity of copper sulfate between the plates is still 0.01 equivalent, but the concentration is 0.2 normal, and, owing to an increase in the fractional ionization, there will be a larger current passing when a potential of 1 volt is applied. The equivalent conductivity is now $100\ I = 37.7$; upon adding 50 c.c. of water, the concentration becomes 0.1 normal, and $100\ I = 43.8$. Correspondingly, if another hundred cubic centimeters of water is added, the concentration is 0.05 normal, and $100\ I$ becomes 51.2; if 300 more is added, $100\ I$ is 62.4; if 500 more is added, so that the concentration is 0.01 normal, $100\ I = 71.7$. Further additions of water will cause a further increase in the current passing. The limit which the conductivity under these conditions approaches as the concentration approaches zero is the equivalent conductivity at zero concentration, or the limiting equivalent conductance. While the actual measurements are not carried out in this way, this will illustrate the meaning of equivalent conductance.

When essentially complete ionization is reached, each ion is free to move independently of the other, and the equivalent conductivity is the sum of two separate values which may be assigned to the separate ions. This is expressed by the equation

$$\Lambda_0 = \Lambda_{0_c} + \Lambda_{0_a}.$$

A method of computing these separate equivalent conductances will be explained later in this chapter.

The limiting value corresponding to complete ionization is not reached even at very low concentration, and it is difficult to make accurate measurements with extremely dilute solutions. However, this limiting value may be obtained by plotting the equivalent conductivity against the concentration, extending or extrapolating the smooth curve thus formed to the axis corresponding to zero concentration, and reading off the value of the intercept. It is this value which is called the equivalent conductivity at zero concentration, and which is written Λ_0. This is not the conductivity of water; it is the limiting value which the equivalent conductivity of the salt approaches at very small concentrations. In these measurements, especially when the solutions are very dilute, the conductivity due to water, or to impurities in it, is subtracted from the measured conductance before computing the equivalent conductivity.

To decrease the uncertainty in extending the curve, it is common practice to plot some function of the conductivity against the concentration, such that the resulting line is nearly straight. Thus Noyes and Falk[1] plot the reciprocal of the equivalent conductivity, $1/\Lambda$, against $(C\Lambda)^n$ and determine by trial the value of n (usually about 0.5) which gives a straight line through the points. Extension of this line to the axis corresponding to $(C\Lambda)^n = 0$ gives the limiting value of $1/\Lambda$, from which Λ_0 is readily obtained. Figure 30 shows how the data for cæsium chloride (Table 67) at 18° are treated by this method, using 0.55 for the exponent. The dotted line of this figure was obtained by using $n = 0.50$, which gives a line somewhat more curved than $n = 0.55$.

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[1] *J. Am. Chem. Soc.*, **34**, 454 (1912).

Many other functions have been proposed for use in obtaining limiting values of the equivalent conductivity, all of which depend upon the principle of plotting some conductivity function against the concentration. The limiting conductances obtained by the various methods[1] agree to within about 1 per cent. For example, the limiting equivalent conductance of potassium chloride at 18° as estimated by any of the methods is between 129 and 130 reciprocal ohms, and the data of Table 66 show that this estimate is substantially correct. It will be observed that the equivalent conductivity increases but little

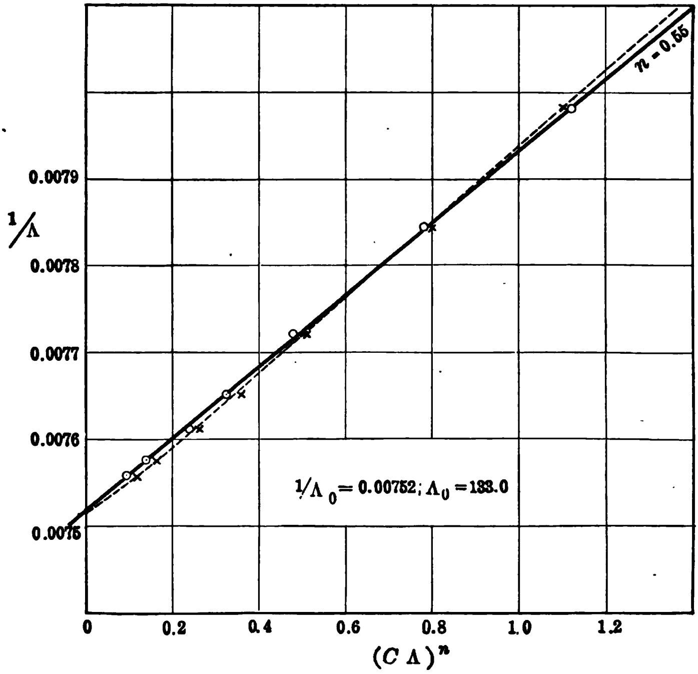

FIG. 30.—Extrapolation of conductivity data.

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[1] Randall, *J. Am. Chem. Soc.*, **38**, 788 (1916); Washburn, *J. Am. Chem. Soc.*, **40**, 145 (1918); **42**, 1,077 (1920); Bates, *J. Am. Chem. Soc.*, **37**, 1,421 (1915); Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1,320 (1913);

below 0.0001 normal, which indicates that ionization is essentially complete at this concentration, at least within about half of 1 per cent.

TABLE 66.—CONDUCTANCE OF POTASSIUM CHLORIDE AT 18°

Equivalent concentration	Equivalent conductance	Fraction ionized
0.000	(129.64)	1.0000
0.00001	129.57	0.9995
0.00002	129.51	0.9990
0.00003	129.45	0.9985
0.00004	129.38	0.9980
0.00005	129.32	0.9975
0.00006	129.26	0.9970
0.00008	129.14	0.9961
0.00010	129.02	0.9953

Weiland, *J. Am. Chem. Soc.*, **40**, 131 (1918).

In Table 67 are given conductivity data for several salts, together with the limiting values obtained as above. This data will be needed in the solution of problems at the end of the chapter, and in the calculations of later chapters.

It should be made clear that the limiting equivalent conductivity is not the conductivity of pure water, though it is often called the equivalent conductivity at zero concentration, or at infinite dilution. In evaluating it the actual conductivity of water is subtracted from the measured conductivity. This value is the limit which the equivalent conductivity approaches as the concentration is diminished and the cross section of the conducting solution increases. It might be computed from an equivalent conductivity at 0.002 normal, together with a freezing point determination at this concentration, to give the fractional ionization. For example, the ionization of potassium nitrate is 96.7 per cent (Table 61) and its equivalent conductivity is 122.5 at 0.002 normal (Table 67). If the ionization should increase to 100 per cent, the equivalent conductivity would increase in the same proportion, and hence should be 122.5/0.967 or 126.7 reciprocal ohms. By extrapolation of conductivity data (Table 67) 126.3 was obtained.

TABLE 67.—EQUIVALENT CONDUCTIVITIES OF SALTS AT VARIOUS TEMPERATURES

Normal Concentration	NaCl		KCl		HCl		$AgNO_3$	LiCl	NH_4OH	Acetic Acid
	18°	25°	18°	25°	18°	25°	18°	18°	18°	18°
0.0000	108.9	127.0	130.0	150.6	380.0	426.0	115.8	98.8	(239)	(350)
0.0001	108.0	.....	129.0	.....	378.1	.....	115.0	98.0	66	107
0.0005	107.1	.....	128.0	.....	377.0	.....	113.9	97.0	38	57
0.0010	106.4	124.1	127.3	.....	375.9	420.4	113.1	96.3	28	41
0.0020	105.5	123.1	126.2	146.6	375.3	418.6	112.1	95.4	20.60	30.20
0.0050	103.7	121.0	124.3	144.0	372.6	415.3	110.0	93.8	13.20	20
0.0100	101.9	118.7	122.4	141.4	369.3	411.6	107.8	92.0	9.60	14.30
0.0200	99.6	115.9	119.9	138.7	365.5	406.7	105.1	89.8	7.10	10.40
0.0500	95.7	111.2	115.7	133.7	358.4	398.4	99.5	86.0	4.60	6.48
0.1000	92.0	106.8	112.0	129.0	351.4	390.4	94.3	82.3	3.30	4.60
0.2000	87.7	101.7	107.9	124.2	342.0	380.2	.....	77.8	2.30	3.24
0.5000	80.9	93.5	102.4	118.8	327.	.....	77.5	70.6	1.35	2.01
1.0000	74.3	.....	98.2	117.4	301.	.....	67.6	63.3	0.89	1.32

Normal Concentration	HNO_3		KNO_3		$Ca(NO_3)_2$	CsCl	Na_2SO_4	$CaCl_2$	HF	$NaNO_3$
	18°	25°	18°	25°	18°	18°	18°	18°	18°	18°
0.0000	376.5	420.0	126.3	145.4	113.7	133.0	111.9	117.4	(361)	105.2
0.0001	.....	.....	125.4	.....	111.9	132.3	109.3	115.2	...	104.5
0.0005	373.9	417.0	124.3	.....	109.9	131.4	106.7	113.3	...	103.5
0.0010	372.9	.....	123.6	.....	108.5	130.7	105.1	112.0	...	102.8
0.0020	371.4	413.7	122.5	140.7	106.5	129.5	103.5	110.1	124	101.8
0.0050	371.0	.....	120.4	.....	103.1	127.5	99.8	106.7	77	99.97
0.0100	365.0	406.0	118.1	134.9	99.5	125.2	95.7	103.4	61	98.07
0.0200	364.0	.....	115.1	.....	95.2	.....	......	99.4	48	95.57
0.0500	353.7	393.3	109.8	126.3	88.4	.....	83.6	93.3	36	91.35
0.1000	346.4	385.0	104.7	120.3	82.5	113.6	77.1	88.2	31	87.16
0.2000	340.0	.....	98.7	.....	76.0	.....	70.0	82.8	28	82.21
0.5000	324.0	.....	89.2	.....	65.7	.....	.....	74.9	27	73.99
1.0000	310.0	.....	80.4	.....	55.9	.....	.....	67.6	26	65.81

Noyes and Falk, *J. Am. Chem. Soc.*, **30**, 454 (1912).

Measurement of Conductivity.—In laboratory practice, the resistance of a solution is measured by means of a Wheatstone Bridge arrangement, using an alternating current of high frequency and a telephone receiver in place of a galvanometer. Such a resistance is chosen for the box that there is a point *b* (Fig. 31) near the middle of the bridge wire *abc* at which there is no sound audible in the telephone receiver. Then the resistance of the box is to that of the cell as the corresponding lengths of the uniform resistance wire *abc*; that is $R_{\text{box}} : R_{\text{cell}} = ab : bc$. The reciprocal of this resistance is the conductivity of the cell, and from its dimensions the specific conductivity can be calculated by means of equation (2); then the equivalent conductivity from equation (3).

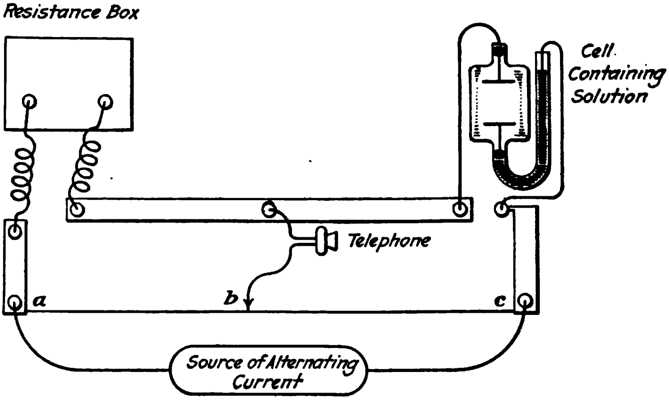

FIG. 31.—Arrangement of Wheatstone bridge for measuring conductivity of a solution.

The purpose of high-frequency alternating current is to avoid electrolysis of the solution during measurement. With frequent reversal of the current direction, any ion which might be deposited upon the electrode one moment would be dissolved from it the next moment.

A convenient form of cell in which to measure the resistances is shown[1] in Fig. 32. Contact with the electrodes is made through a glass seal into the tubes filled with mercury. Solution is drawn into the cell as into a pipet. As the electrodes are sealed up inside a glass vessel, they cannot be moved, and so alter the dimensions of that part of the solution between the electrodes. The electrodes are coated

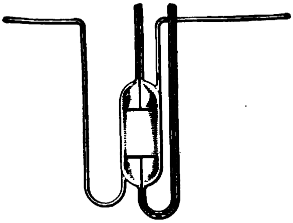

FIG. 32.—Conductance cell, pipet type.

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[1] Washburn, *J. Am. Chem. Soc.*, **38**, 2,449 (1916).

with platinum black to increase their surface, and eliminate polarization.[1]

Conductivity of Pure Water.—As stated above, the conductance of the water used in preparing a solution is subtracted from the measured conductance in determining that due to the salt. Careful experiments have shown that water is itself ionized to a slight extent, such that at 25° the concentration of hydrogen ion (and of hydroxide ion as well) is 0.0000001 normal. It is not from this source that most of the error in measuring conductivities of dilute solutions arises, but from the presence of dissolved impurities. Even after careful distillation, water may contain ammonia and carbon dioxide; and it will dissolve sodium and calcium salts from the glass in which it is contained in a very short time. Perfectly pure water has a specific resistance of 25,000,000 ohms, ordinary distilled water a specific resistance of 100,000 ohms perhaps, and a good quality of "conductivity water," from 1,000,000 to 10,000,000 ohms. Water of a resistance greater than a million ohms per centimeter cube cannot be preserved in glass for more than a very few hours; perhaps for a day or so in quartz vessels. For this reason, conductivity water is freshly prepared for a set of measurements, first by distillation in the usual way, then by a second distillation (often directly into the conductivity apparatus) from alkaline permanganate solution, rejecting the first third of the distillate.

Extent of Ionization.—If the conduction of electricity through a solution is due to the motion of ions bearing definite charges under an applied electrical potential, and if the ions have characteristic velocities corresponding to a potential gradient of 1 volt per centimeter, the increase in equivalent conductivity at increasing dilution would appear to be due to an increase in the quantity of the conducting ions. This is exactly what the freezing point determinations show in dilute solutions, namely, that the fraction of a salt in the ionized condition is greater as the concentration decreases. If the velocity of a particular ion is the same under the same potential gradient in a dilute solution as in (practically) pure water, then the ratio of the equivalent conductivity to the limiting value of it, Λ_c/Λ_0, should be a measure of the fraction of a salt ionized at any selected concentration. This statement involves the assumption that the frictional resistance opposing the motion of ions is the same in a solution as in pure water, *i.e.*, that ions have characteristic velocities which change but little as the concentration of salt is varied. Partly owing to slight variations (usually less than 1 per cent) in the values of the limiting conductance, Λ_0, as computed by various extrapolation methods from the same data, there is not complete agreement as to the fractional ionization indicated by this method. But as shown in Table 68 there is usually no large difference between degrees of ionization computed from freezing point data and corresponding figures from the conductivity ratio. This is evidence in favor of the correctness of the belief that increasing equivalent conductivity with decreasing concentration is due to increased ionization, and not to an increase in the velocity of ions already formed. Such differences as appear in Table 68 are not to be explained as experimental error, however. There is a real difference which is far in excess of the possible errors in the measurements. Some of the ionization values derived from conductivity ratios are brought into closer accord with those from freezing point data when the viscosity of a solution is taken into account in computing the conductivity ratio. Other cases of divergence are not eliminated in this way however, and a complete explanation of the differences must await the results of future work.

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[1] Much work has been done recently in perfecting the apparatus for measuring conductivity, and each feature of the apparatus has been given careful study with a view to eliminating experimental errors. Clearly, nothing was to be expected in advancing the theory of electrolytes when there was uncertainty in the data. The best critical reviews are those of Washburn, *J. Am. Chem. Soc.*, **35**, 177 (1913); **38**, 2,431 (1916); **40**, 106 (1918), and of Acree, *Ibid.*, **39**, 235 (1917). For a discussion of the preparation of water of sufficient purity see Kendall, *J. Am. Chem. Soc.*, **39**, 9, (1917) and Weiland, *J. Am. Chem. Soc.*, **40**, 131 (1918).

Salts of the same ionic type, for example, those which give a positive ion bearing a single charge and a negative ion with a single charge (like potassium chloride, ammonium nitrate, lithium bromide and sodium iodide) are ionized to about the same extent at equal concentrations, but salts of different types ionize to different extents. This is illustrated in Table 69, for several typical salts. The limiting equivalent conductances

TABLE 68.—COMPARISON OF PERCENTAGE IONIZATION[1] AS CALCULATED FROM FREEZING POINT DEPRESSIONS (F.P.) AND FROM CONDUCTANCE RATIOS (C.R.)

		Equivalent concentration						
Salt	Method	0.005	0.01	0.02	0.05	0.10	0.20	0.50
KCl.........	F. P.	96.3	94.3	91.8	88.5	86.1	83.3	80.0
	C. R.	95.6	94.1	92.2	88.9	86.0	82.7	77.9
NaCl	F. P.	95.3	93.8	92.2	89.2	87.5	85.0	82.4
	C. R.	95.3	93.6	91.6	88.2	85.2	81.8	77.3
NH_4Cl	F. P.	94.7	92.8	90.7	87.8	85.6	83.2	...
	C. R.	....	94.1	92.1	....	....	....	...
$NaNO_3$......	F. P.	....	90.3	88.5	85.5	83.0	79.8	...
	C. R.	95.0	93.2	91.0	87.1	83.2	78.8	71.9
$KClO_3$.......	F. P.	....	91.4	89.1	84.9	79.8	....	...
	C. R.	95.2	93.3	91.0	86.6	82.7	78.0	70.3
$BaCl_2$........	F. P.	89.7	87.8	85.5	81.9	78.8	75.8	...
	C. R.	....	88.3	85.0	79.8	75.9	72.0	67.2
$MgCl_2$.......	F. P.	....	....	88.5	85.4	83.9	83.3	...
	C. R.	91.0	88.3	85.1	80.3	76.5	72.8	68.7
$Pb(NO_3)_2$....	F. P.	89.0	85.0	80.4	72.4	64.9	56.8	42.7
	C. R.	88.6	84.5	79.3	70.8	63.5	55.9	45.4
$MgSO_4$	F. P.	69.4	61.8	53.6	42.0	32.4	22.3	8.4
	C. R.	74.0	66.9	59.6	50.6	44.9	40.3	...
$CuSO_4$.......	F. P.	61.6	54.5	45.5	31.8	....	....	...
	C. R.	70.9	62.9	55.0	45.5	39.6	35.1	

from which the conductivity ratios were derived have been obtained by extrapolating a different function, but using the same experimental data as were employed for Table 68. Comparison of ionization values in these two tables will therefore show

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[1] Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 485 (1912).

TABLE 69.—PERCENTAGE IONIZATION OF TYPICAL SALTS[1]

Salt	Concentration									
	0.0001	0.0002	0.0005	0.001	0.002	0.005	0.01	0.02	0.05	0.1
KCl	99.2	99.0	98.5	97.9	97.1	95.6	94.1	92.2	88.9	86.0
$LiIO_3$	99.1	98.7	97.9	97.0	95.8	93.6	91.2	88.3	83.4	78.9
$MgCl_2$	98.4	97.8	96.7	95.5	93.9	91.0	88.3	85.1	80.3	76.5
$Ba(NO_3)_2$	98.4	97.8	96.7	95.3	93.4	89.8	86.1	81.8	74.4	67.9
Tl_2SO_4	....	....	96.4	94.8	92.4	88.2	83.7	78.0	69.4	62.5
$PbCl_2$	....	....	96.0	94.3	91.7	86.5	80.8	73.8	62.7	
$CuSO_4$	96.1	94.4	90.5	86.2	80.4	70.9	62.9	55.0		

that there is no essential difference between the limiting equivalent conductances based upon different extrapolation equations.

Mercuric halides and cadmium halides are not as highly ionized as other salts of their ionic type, but the explanation of these exceptions is not yet known.

Ionization of Acids and Bases.—The general statement just made in regard to ionization of salts of a given type does not apply at all to acids and bases, which show the greatest variation in their ionization. Thus while sodium nitrate and sodium acetate are almost equally ionized, nitric acid ionizes in one-tenth normal solution about 92 per cent and acetic acid at the same concentration is ionized slightly more than 1 per cent. Mineral acids and bases, like hydrochloric, nitric and sulfuric acids, potassium and sodium hydroxides, ionize to about the same extent as their salts, but other acids and bases are much less ionized than their salts. Hydrofluoric acid, which might be expected to ionize like hydrochloric acid, is exceptional in its ionization, as in its other properties. No general rules can be given, more than has been said above, from which to predict the ionization of an acid. Organic acids are usually only slightly ionized, and become more so when halogens are substituted in them; thus trichloracetic acid is ionized about like hydrochloric acid, monochloracetic acid is considerably less ionized, though more so than acetic acid. Some typical results are shown below.

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[1] Randall, *J. Am. Chem. Soc.*, **38**, 790 (1916).

TABLE 70.—PERCENTAGE IONIZATION OF ACIDS AND BASES; AS CALCULATED FROM THE CONDUCTIVITY RATIOS

Concentration	KOH	HCl	HF	HNO_3	NH_4OH	$HC_2H_3O_2$
0.001	....	99.0	..	99.0	11.7	11.7
0.002	98.0	98.6	34	98.6	8.6	8.6
0.005	97.5	98.1	21	....	5.5	5.7
0.010	96.3	97.2	17	96.9	4.0	4.1
0.020	93.9	95.7	13	....	3.0	3.0
0.050	92.5	94.4	10	93.8	1.9	1.8
0.100	91.0	92.0	9	92.0	1.4	1.3
0.500	88.0	89.0	7	....	0.6	0.6
1.000	87.0	84.0	6	....	0.4	0.4

Viscosity Correction.—On account of the high viscosity of some solutions, it has often been stated that the ions encounter a greater resistance in moving through them. For example, a normal solution of lithium chloride has a viscosity 15 per cent greater than pure water; hence this solution should offer a greater resistance to the motion of lithium ions and chloride ions moving through it. If the increased resistance is proportional to the increase in viscosity, a better measure of the fractional ionization would be obtained by allowing for this effect. Thus in place of Λ/Λ_0, this ratio is multiplied by the relative viscosity, *i.e.*, η/η_0, and the expression for fractional ionization is

$$\gamma = \frac{\Lambda}{\Lambda_0}\frac{\eta}{\eta_0}.$$

In many cases the fractional ionizations so calculated are in better agreement with those from freezing point depressions than the conductivity ratios without a viscosity correction; but in other cases the agreement is not so good. It is not yet agreed which procedure gives a better measure of ionization, and we shall not introduce viscosity corrections into our calculations. This does not mean that they are useless, for some such correction is doubtless required; but until the method of making this correction rests on a more established basis, it appears to be an unnecessary refinement.[1]

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[1] This correction is discussed fully by Washburn, *J. Am. Chem. Soc.*, **33**, 1,462 (1911), giving full references to the earlier literature on the subject.

Conductance and Ion Velocities.—Since the passage of positive electricity in one direction is, so far as an electric current is concerned, equivalent to the passage of an equal amount of negative electricity in the opposite direction, the total electricity carried through a cross section of solution by its ions is equal to the sum of the equivalents of positive ion (cation) and of negative ion (anion) passing in their respective directions. That is, if N is the total number of faradays of electricity passing, and N_c and N_a are respectively the number of equivalents of positive and of negative ion crossing a given section,

$$N = N_c + N_a \tag{4}$$

Let us consider first the positive electricity alone, that carried by positive ions in a solution containing C equivalents per liter, in a tube of cross section q and length l, to which a potential of E volts is applied, and let γ represent the fractional ionization of the salt. When all of the positive ions have moved one centimeter, the quantity of positive electricity which has crossed a given line is equal to the charge upon all the positive ions in q cubic centimeters of the solution, or $(C\gamma/1000)q$. The electricity passing on the positive ions per second is the product of this quantity and the distance moved by each positive ion per second, or

$$\text{Equivalents per sec.} = \frac{N_c}{t} = \frac{C\gamma}{1000}qV_c \tag{5}$$

where V_c is the velocity of the positive ion. But $V_c = U_c\frac{E}{l}$, where U_c is the velocity under unit potential gradient, and E/l is the potential gradient. In t seconds the total quantity of positive ion crossing a given line is

$$N_c = \frac{C\gamma}{1000}qtU_cE/l \tag{6}$$

A similar expression containing U_a, the velocity of the negative ion, shows the quantity of negative electricity passing, and the total quantity is given by

$$N = N_c + N_a = \frac{C\gamma}{1000}qt(U_c + U_a)\frac{E}{l} \tag{7}$$

The current, I, is coulombs passing per second, and is by Ohm's law equal to E/R or to its equivalent EL'. If we denote by F the value of a faraday or 96,500 coulombs, the coulombs per second is NF/t. The current flowing is obtained by multiplying both sides of equation (7) by $\frac{F}{t}$.

$$I = \frac{NF}{t} = \frac{C\gamma}{1000} Fq(U_c + U_a)\frac{E}{l} \tag{8}$$

The specific conductivity is equal to $L'l/q$, or since $I = EL'$, it follows from equation (8) that

$$L = \frac{C\gamma}{1000}(U_c + U_a)F. \tag{9}$$

Upon substituting in this equation the relation $1000\ L = C\Lambda$, from equation (3), and putting for γ its equal $\frac{\Lambda}{\Lambda_0}$, we obtain

$$(U_c + U_a)\,F = \Lambda_0 \tag{10}$$

from which it is possible to calculate the mobilities of the ions when we know the fraction of the equivalent conductivity due to each ion. (A method of obtaining this fraction will be taken up in the next paragraph.) For instance in potassium chloride the ionic velocities are nearly equal, though the ions move in opposite directions of course. Assuming them equal, we may calculate the velocity U from the limiting value of the equivalent conductivity, $\Lambda_0 = 130$, since $2UF = 130$, and it follows that $U = \frac{130}{2 \times 96{,}500} = 0.000674$ cm. per second. This will give an idea of the velocity of an ion toward an electrode when the potential applied is 1 volt for each centimeter between electrodes.

Velocity Ratios for The Ions. Transference Numbers.—It might seem at first thought that all the ions move through a solution with the same velocity, since they are discharged at the electrodes in equivalent quantities. But this is not the case, for ions may arrive in the vicinity of the electrodes faster or slower than they are needed for discharge; the solution around the electrode thus changing its concentration. Further evidence of different ionic velocities is furnished by the fact that the equivalent conductivities of substances which are ionized to about the same extent are widely different. Thus for 0.1 normal solutions of sodium acetate and hydrochloric acid, which are about equally ionized, the equivalent conductivities at 18° are 72 and 350 respectively.

This difference in ionic velocities may be illustrated by considering the results of an actual experiment. The U-tube of Fig. 33 contains dilute hydrochloric acid, is fitted with a silver anode and a platinum cathode, and is surrounded by a constant temperature bath and otherwise so treated that stirring of the solution is avoided, while one faraday of electricity passes through it. The solution is then withdrawn in three portions as shown by the dotted lines, and these are analyzed separately.

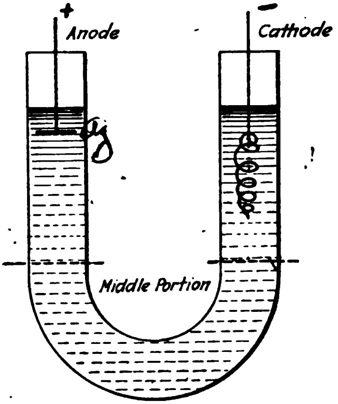

Fig. 33.—Diagram of transference apparatus.

It will be found that the concentration of the middle portion has not changed during the electrolysis, which shows that the quantity of hydrogen ion entering this portion from the anode region is equal to the quantity which has left the middle portion and entered the cathode portion; also the quantity of chloride ion entering the middle portion from the cathode region is equal to the quantity which has left the middle and entered the anode portion. The anode portion has lost one equivalent of chloride ion during the electrolysis according to the anode reaction

$$\text{Ag (solid)} + \text{Cl}^- = \text{AgCl (solid)} + \ominus$$

where the symbol $\ominus$ indicates one faraday of negative electricity. But any portion of solution must at all times contain the same number of equivalents of positive ion as of negative ion; hence the loss of hydrogen ions into the middle portion plus the gain of chloride ions from the middle portion are together equal to one equivalent, the loss of negative ions by electrolysis. That is, the anode portion has lost one equivalent of negative ion by electrolysis; it has gained part of an equivalent of chloride ion from the middle portion, and it has lost the remainder of an equivalent of positive ion to the middle portion. Equal quantities of positive and negative ions are therefore still present.

Analysis shows that the quantity of hydrochloric acid in the anode portion has decreased 0.828 equivalents. But by electrolysis the anode portion lost one whole equivalent of chloride ion and no hydrogen ion. Then 0.172 (*i.e.*, 1 − 0.828) equivalents of chloride ion must have come into the anode portion from the middle portion and 0.828 equivalents of hydrogen ion must have gone out of the anode portion. Since both ions are under the same potential gradient, being in the same solution, their velocities bear the ratio of these quantities of ion lost, *i.e.*,

$$U_{\mathrm{H}} : U_{\mathrm{Cl}} = 0.828 : 0.172.$$

Let us now consider the cathode portion, where analysis shows that 0.172 equivalents of hydrochloric acid have been lost during the experiment. Hydrogen gas was evolved by the electrochemical reaction,

$$H^+ = \tfrac{1}{2}H_2 + \oplus$$

and one equivalent of hydrogen ion was used up. But the loss in hydrogen ion as shown by analysis was only 0.172 equivalents, hence 1 − 0.172, or 0.828 equivalents of hydrogen ion must have entered from the middle portion. This is just the quanitty of hydrogen ion which entered the middle portion from the anode region, hence the middle portion has gained no hydrogen ion and lost none. Analysis showed the loss of 0.172 equivalents of chloride ion from this cathode portion, none of which entered into the electrolytic reaction. This therefore entered the middle portion, and it is equal to the quantity of chloride ion which entered the anode portion from the middle. But the ratio of hydrogen ion passing through the middle portion to the chloride ion passing through it is the ratio of their velocities, *i.e.*,

$$U_{\mathrm{H}} : U_{\mathrm{Cl}} = 0.828 : 0.172$$

These figures, being obtained from experiments in which the transfer of electrolyte from one portion of a solution to another is determined, are commonly called the transference numbers of the ions; ionic velocity ratios would be a more suitable term.

The transference number of an ion is the fraction of the total electricity carried by it through a solution. A table of such transference numbers for the positive ions in solution is shown in Table 71. It should be noted that these transference numbers change but little with the temperature, in spite of the large increase in equivalent conductivity at higher temperatures mentioned on page 178. This means that all ions increase their velocities at about the same fractional rate as the temperature is raised, but there is a slight change in ionic velocity ratio with concentration, which lacks an explanation as yet. If the ions moved through solutions at the same rate as through pure water there should be no such change; it is commonly ignored in calculations, but is still one of the unsolved problems of physical chemistry. A possible cause of the change is that one ion

TABLE 71.—TRANSFERENCE NUMBERS OF POSITIVE IONS

Salt	Temperature	Concentration					
		0.005	0.01	0.02	0.05	0.10	0.20
$NaCl$	0°	0.387	0.387	0.387	0.386	0.385	
	18	0.396	0.396	0.396	0.395	0.393	0.390
	30	0.404	0.404	0.404	0.404	0.403	
KCl	0°	0.493	0.493	0.493	0.493	0.492	0.491
	18	0.496	0.496	0.496	0.496	0.495	0.494
	30	0.498	0.498	0.498	0.498	0.497	0.496
$LiCl$	18	.....	0.332	0.328	0.320	0.313	0.304
NH_4Cl	18	.....	0.492	0.492	0.492		
$AgNO_3$	18	.....	0.471	0.471	0.471	0.471	
	30	0.481	0.481	0.481	0.481	0.481	0.481
HCl	0°	0.847	0.846	0.844	0.839	0.834	
	18	0.832	0.833	0.833	0.834	0.835	0.837
HNO_3	20	0.839	0.840	0.841	0.844		
$BaCl_2$	0°	0.439	0.437	0.432			
	25	.....	.....	.....	0.438	0.427	0.415
$Ba(NO_3)_2$	25	.....	.....	.....	0.456	0.456	0.456
$MgSO_4$	18	0.388	0.385	0.381	0.373		
$CuSO_4$	18	.....	.....	0.375	0.375	0.373	0.361
K_2SO_4	18	.....	0.494	0.492	0.490		
	25	.....	.....	.....	0.496	0.494	0.493
H_2SO_4	20	.....	.....	0.822	0.822	0.822	0.820
Na_2SO_4	18	.....	0.392	0.390	0.383		
$CaCl_2$	20	0.440	0.432	0.424	0.413	0.404	0.395

Noyes and Falk, *J. Am. Chem. Soc.*, **33**, 1,454 (1911).

combines with more water than the other, thus increasing its size and decreasing its velocity. There is definite proof that the ions are combined with considerable water[1] and it is reasonable to suppose that the extent of this solvation changes with the proportion of water available, and with the temperature. Doubtless other factors also exert an influence.

If the tube of Fig. 33 is filled with sodium chloride, sodium hydroxide forms at the cathode, and no sodium is lost from the tube; the reaction of chloride ion at the silver anode is the same as with hydrochloric acid. Analysis shows that the net loss of chloride ion from the anode portion of a tube of sodium chloride is 0.398 equivalents per faraday of electricity passed. Since a whole equivalent of chloride ion is lost by electrolysis, it follows that $1 - 0.398 = 0.602$ equivalents of chloride ion have entered the anode portion for each faraday of electricity passed. The quantity of electricity carried through the middle portion by chloride ions is therefore about 60 per cent of the total, and only 40 per cent has been carried by the positive ions. It should be remembered that the transference number of sodium ion in a solution of sodium chloride is not the same as in a solution of sodium nitrate or sodium acetate. This number is the fraction of the total electricity carried by the positive ion, which moves with a characteristic velocity; whether the fraction carried by this ion is greater or less than half will depend on whether the characteristic velocity of the other ion is less or greater than that of sodium ion.

In calculating transference numbers from actual experimental data, there should be tabulated for each portion of solution, first the change in each constituent due to electrolysis, then the net change found by analysis, and finally, the change in each substance due to transference. A faraday is a very large quantity of electricity, and experiments are commonly carried out with a much smaller quantity. The total electricity passed through a solution is measured by a silver coulometer placed in series with the transference apparatus. Since the electrolysis and transference changes are both strictly proportional to the quantity of electricity passed, the values per faraday are calculated by simple proportion.

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[1] Washburn and Millard, *J. Am. Chem. Soc.*, **37**, 694 (1915).

A transference number is the ratio of the quantity of electricity carried by the ion to which it applies, divided by the total quantity of electricity. As each equivalent of ion has the same electric charge as that of every other ion, the transference number is the ratio of the velocity of one ion to the sum of the velocities of the two ions,

$$T_c = \frac{U_c}{U_c + U_a}$$

Each mobility is proportional to its limiting equivalent conductivity, hence a transference number is also given by the ratio

$$T_c = \frac{\Lambda_c}{\Lambda_c + \Lambda_a}.$$

Conductances of The Separate Ions.—It has already been explained that each salt approaches a limiting equivalent conductance as the concentration decreases. In very dilute solutions, where this limit is essentially reached, each ion is free to move about as if no other ions were present. From the ionic velocity ratios obtained above, and from the limiting conductance, may be calculated the equivalent conductance of each ion in a solution. Thus the limiting equivalent conductance for sodium chloride at 18° is 108.9, and if this is multiplied by the transference number for sodium ion calculated above, 0.398, the result is 43.4 for the limiting conductance of the sodium ion, and 108.9 − 43.4 or 65.5 for chloride ion.

The limiting conductance for sodium nitrate is 105.2, 43.4 of which is due to sodium ion. Hence the equivalent conductance of nitrate ion is 105.2 − 43.4 = 61.8. For potassium nitrate the limiting value is 126.3, hence 126.3 − 61.8 = 64.5 is the equivalent conductance of potassium ion. The limiting value for potassium chloride should then be the sum of the values for potassium ion and chloride ion found above or 64.5 + (108.9 − 43.4) = 130. Proceeding in this way, it is possible to calculate a value characteristic of each ion at each temperature.

In Table 72 the limiting equivalent conductances of the separate ions at several temperatures are shown.[1] From these values the conductance of any solution involving these ions may be calculated at any temperature by making a suitable estimate of the fractional ionization. It is to be noted that this fractional ionization changes only slightly with the temperature, and that it decreases at higher temperatures.

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[1] Johnston, *J. Am. Chem. Soc.*, **31**, 1,010 (1909).

TABLE 72.—LIMITING CONDUCTANCES OF IONS

Ion	Temperature							
	0	18	25	50	75	100	128	156
K^+	40.4	64.6	74.5	115	159	206	263	317
Na^+	26.0	43.5	50.9	82	116	155	203	249
NH_4^+	40.2	64.5	74.5	115	159	207	264	319
Ag^+	32.9	54.3	63.5	101	143	188	245	299
½ Ba^{++}	33.	55.	65.	104	149	200	262	322
½ Ca^{++}	30.	51.	60.	98	142	191	252	312
Cl^-	41.1	65.5	75.5	116	160	207	264	318
NO_3^-	40.4	61.7	70.6	104	140	178	222	263
$C_2H_3O_2^-$	20.3	34.6	40.8	67	96	130	171	211
½ SO_4^{--}	41.	68.	79.	125	177	234	303	370
H^+	240.	314.	350.	465	565	644	722	777
OH^-	105.	172.	192.	284	360	439	525	592

The equivalent conductances for some other ions at 18° are Li^+ 33.3, ½Pb^{++} 60.8, ½Mg^{++} 46, ½Zn^{++} 47, Br^- 67.7, I^- 66.6, F^- 46.7, BrO_3^- 48.

Change of Conductivity with Temperature.—The equivalent conductivity at any concentration changes rapidly with temperature, in the way shown in Table 73. For very dilute solutions the change is a linear increase of about 2 per cent per degree rise of temperature; but stronger solutions increase with temperature at a decreasing rate, as shown[1] in Fig. 34. This effect is due to a decrease in the fractional ionization at high temperature, which counterbalances the effect of increased velocities of the ions. For a solution which is half-normal there is a point of maximum equivalent conductivity at about 250°, above which the effect of decreased ionization is greater than that of increased ionic velocity. Conductivities of solutions above the boiling point of water are made in a closed steel vessel capable of withstanding the pressure necessary to keep the solvent liquid.

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[1] Noyes and Coolidge, *J. Am. Chem. Soc.*, **26**, 165 (1904).

TABLE 73.—CHANGE OF EQUIVALENT CONDUCTANCE WITH TEMPERATURE[1]

Salt	Equivalent concentration	Equivalent conductivity at				
		18°	140°	218°	281°	306°
NaCl.	0.0000	110.30	512	782	984	1078
	0.0005	107.18	493	747	926	1004
	0.0020	105.55	482	726	893	960
	0.0100	101.95	461	686	830	878
	0.1000	92.02	403	577	656	643
KCl.	0.0000	131.40	572	845	1041	1125
	0.0005	128.11	. . .	. . .	. . . . .	1051
	0.0020	126.31	538	786	950	1007
	0.0100	122.43	. . .	. . .	. . .	922
	0.1000	112.03	447	620	699	686

As the viscosity of water decreases rapidly with increasing temperature, the "fluidity" (reciprocal of the viscosity) increases. This rate of increase is about the same as the rate at which conductivity increases. Recalling that conductivity is the reciprocal of resistance, it is seen that the decreased resistance of electrolytes

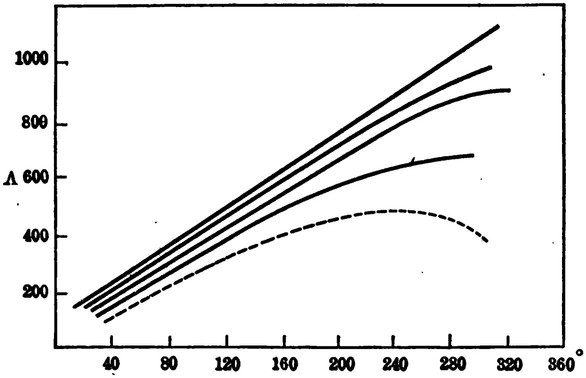

FIG. 34.—Change of equivalent conductance of sodium chloride with increasing temperature. The top line is Λ_0, the next lines are for 0.002, 0.01 and 0.1 normal; the dotted line is for half normal.

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[1] Noyes and Coolidge, *J. Am. Chem. Soc.*, **26**, 134 (1904); Johnston, *J. Am. Chem. Soc.*, **31**, 1,010 (1909).

nearly parallels the decrease in resistance to flow of the water. Hence it is very probable that the increase in equivalent conductivity is largely due to the decrease in resistance to the motion of ions through water.

Calculation of Conductivity.—From equation (3) the relation between equivalent and specific conductivity is obtained. In Table 69 the fractional ionization is shown for salts of various types, and that of salts not shown may be estimated from the ionization of other salts of its type. By combining with equation (3) the relation $\gamma = \frac{\Lambda}{\Lambda_0}$, and noting that γ is obtainable from table 69, we have then the equation

$$1000L = C\gamma\Lambda_0 \tag{11}$$

from which the specific conductivity of a solution at any temperature may be calculated by means of the limiting values of separate ions in Table 72. When such a calculation is desired for a temperature between those given, linear interpolation will give satisfactory results. For example, potassium nitrate in 0.1 normal solution may be expected to ionize to the same extent as potassium chloride, 86 per cent; the limiting conductances of its ions at 25° are 74.5 and 70.6. Then 86 per cent of the sum of these values, 124.8, is the equivalent conductivity, and 0.01248 is the specific conductivity. Its reciprocal is 81.0, the specific resistance of the solution; the measured specific resistance is 83 ohms. This represents about the average precision to be obtained in such calculations; often the agreement is much better, sometimes it is not so good. We have at least a useful method of calculating resistances where great accuracy is not desired.

Hydration of Ions.—Mention has often been made of some peculiarity in the behavior of a solution as due to hydration, or a loose combination between solute and solvent. Thus the fractional ionization of potassium chloride calculated from depressions of freezing points (Table 61) is not in agreement with that from the conductivity ratio (Table 69); and neither set of figures accords with those in Table 63 calculated from vapor pressure lowering. The osmotic pressures of lithium chloride solutions could not be used for satisfactory ionization calculations. Transference numbers are often found to change slightly with the concentration, probably on account of changing hydration. All of these effects are comparatively small, but they are not due to errors in the experimental data. In rough calculations these deviations are ignored, but much careful work has been done in seeking an explanation of them. No general explanation has been found, but hydration is certainly one of the factors responsible for some of the observed facts. We have no reliable method for determining the quantity of water combined with solute in a solution, though much work has been done in connection with freezing point deviations,[1] and in other ways. There is, however, a method for determining whether the two ions of a solute carry different quantities of water or not, and this may be used to calculate the quantity of water combined with one ion if the other is *assumed* to carry none. Thus, suppose a transference experiment to be conducted upon a solution of sodium chloride to which has been added a little sugar. Sugar is not an ionized substance, it does not move through a solution when electricity is passed, and if at the end of an experiment the ratio of sugar to water in the electrode portions has changed, water must have come into this portion on the anion, or have been carried out of it on the cation.

When a faraday of electricity passes through a normal solution of sodium chloride, 0.76 mols of water are lost from the anode portion, as shown by a change in the ratio of sugar to water. Assuming that the chloride ion does not carry any water, these 0.76 mols of water must have been carried out by 0.38 equivalents of sodium ion, this being the quantity of sodium ion leaving the anode portion per faraday passed. That is, each sodium ion is associated with two molecules of water, since 0.38 equivalents carried away 0.76 mols of water. There is, however, no ground for the assumption that chloride ions carry no water, but only the experimental fact that water has disappeared from the anode portion. Let us assume that a chloride ion carries four molecules of water. For each faraday of electricity passed, there are 0.62 equivalents of chloride ion entering the anode portion; these would bring in 0.62 × 4 = 2.48 mols of water. But there was a net loss of water, not a gain. Sodium ions have carried out 0.76 mols more water than chloride ions brought in, that is 2.48 + 0.76 = 3.24 mols, and this quantity of water moved on 0.38 equivalent of sodium ion. Hence 3.24/0.38 = 8.5 mols of water per sodium ion, if the chloride ion carries four mols of water. This method gives only the difference in hydration, the actual hydrations here calculated are based on some definite *assumption* as to the hydration of chloride ions; not on an experimentally established hydration of it. But as chloride ions cannot carry less than no water at all, two molecules on each sodium ion is the lower limit of its hydration. Table 74 shows some results of such calculations. The mols of water moved per faraday of electricity are the result of experiment, based on the fact that sugar is not transported by an electric current; calculated values of hydration were made as explained above.

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[1] Jones and others, *Publ. Carnegie Inst.*, **60**, (1907). His data were calculated on the assumption that all deviations from the laws of ideal solutions were due to hydration of the solute, and led to the conclusion in some strong solutions (chromic acid for example) that all of the water present was combined. This is of course absurd, for there could then be no solvent, but only solute. A review of hydration in general is given by Washburn, *Technology Quarterly*, **21**, 360 (1908), together with a criticism of each method.

TABLE 74.—HYDRATION OF IONS[1] IN NORMAL SOLUTION

Salt	Mols water carried from anode to cathode per faraday of electricity	Transference number of positive ion	Mols water on positive ion when chloride ion is assumed to have		
			0	4	10
HCl	0.24	0.844	0.3	1.0	2.1
CsCl	0.33	0.491	0.7	4.7	11.0
KCl	0.60	0.495	1.3	5.4	11.5
NaCl	0.76	0.383	2.0	8.4	18.0
LiCl	1.50	0.304	4.7	14.0	28.0

The problem of solvation in general is still far from solved, though it is of the greatest importance in connection with the properties of solutions in general. There appears to be an intimate connection between the process of ionization itself and an affinity for water. It has been suggested that ionization is preceded by combination with the solvent, and that the fractional ionization is proportional to the extent of the attraction between water and the dissolved substance,[1] but this view is not universally accepted.

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[1] Washburn and Millard, *J. Am. Chem. Soc.*, **37**, 694 (1915).

Activity of Ions.—There is a method based on electromotive force measurements, to be described in a later chapter, for determining the effective ion concentration in chemical equilibrium, and in producing an electromotive force in a cell. This effective concentration so determined is called the "activity" of the ion. If the salt concentration is divided into this "activity," a fraction is obtained which does not agree with ionization values derived from freezing point or conductivity experiments for the same solute. The differences are not to be ascribed to experimental error, but to a fault in the fundamental ionic theory, for which no explanation is yet available. Table 75 shows the extent of these differences; the columns headed "activity coefficients" give the values based upon electromotive force measurements.[2]

TABLE 75.—COMPARISON OF ACTIVITY COEFFICIENTS AND CONDUCTANCE RATIOS

Mols of salt per 1,000 gram of water	Activity Coefficients				Conductance ratios			
	KCl	LiCl	HCl	KOH	KCl	LiCl	HCl	KOH
0.001	0.979	0.976	.....	.....	0.979	0.976	0.990	
0.003	0.943	0.945	0.990	0.982	0.968	0.962	0.986	0.980
0.005	0.923	0.930	0.965	0.975	0.956	0.949	0.981	0.975
0.010	0.890	0.905	0.932	0.961	0.941	0.932	0.972	0.963
0.030	0.823	0.848	0.880	0.920	0.914	0.904	0.957	0.939
0.050	0.790	0.817	0.855	0.891	0.889	0.878	0.944	0.925
0.100	0.745	0.779	0.823	0.846	0.860	0.846	0.925	0.910
0.200	0.700	0.750	0.796	0.793	0.827	0.812	0.909	0.891
0.300	0.673	0.738	0.783	0.769	0.807	0.792	0.903	0.889
0.500	0.638	0.731	0.773	0.765	0.779	0.766	0.890	0.884
0.700	0.618	0.734	0.789	0.772	0.761	0.751	0.874	0.879
1.000	0.593	0.752	0.829	0.786	0.742	0.737	0.845	0.877

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[1] Kendall, *J. Am. Chem. Soc.*, **36,** 1,069 (1914); Dhar, *Z. Elektrochemie*, **20,** 57 (1914); Bousfield, *Trans. Faraday Soc.*, **15,** 73 (1919).

[2] Noyes and MacInnes, *J. Am. Chem. Soc.*, **42,** 239 (1920); Similar results have been calculated by Lewis and Linhart, *J. Am. Chem. Soc.*, **41,** 1,951 (1919).

There is probably no experimental error as large as a tenth of 1 per cent involved in these measurements; but a comparison of the figures for any solute will show differences many times this. Thus for 0.2 normal hydrochloric acid, the difference is 11 per cent, for 0.3 normal potassium hydroxide it is 12 per cent. This serious difference has led to a new proposal[1] that *ionization in these solutions is essentially complete* and that decreased activity, conductivity-ratio changes, and freezing point changes with concentration are due to some other cause. So far this other cause has not been discovered, and it would be useless under the circumstances to discuss the new theory fully here. However, it is obvious that some alteration in the ionic theory is needed to explain these discrepancies, and any such change must be given a fair hearing. For the present treatment, we shall assume that the conductivity ratio gives an essentially reliable method of measuring fractional ionization. In doing this we do not presume to decide whether ionization is complete or not; we only follow an older and commonly accepted usage while awaiting further experiments bearing on the new hypothesis. Some alteration in the ionic theory is urgently needed to explain many puzzling facts, but it is not yet clear that this hypothesis is the desired change.

Ionization in Solvents Other Than Water.—Much scattered data exists on the ionization of substances in non-aqueous solvents,[2] but the conclusions stated in connection with experiments of various authors are often considerably at variance. Until more information is at hand, an attempt to treat the general subject of non-aqueous solutions would be out of place.

A thorough study of ionization and electrical conductivity has been made upon anhydrous formic acid solutions;[3] and such solutions appear to be somewhat less complex in their behavior than water solutions. Thus the ion concentration calculated from the conductance ratio is identical with the effective concentration or activity, and the ions and non-ionized molecules exhibit approximately the behavior of ideal solutes. The fractional ionization decreases in strong solutions in a regular manner, limiting equivalent conductivities are obtained in the same way as for water solutions; equivalent conductivities are of the same order of magnitude as those in water. A table of data for these solutions is here given.

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[1] Noyes and MacInnes, *J. Am. Chem. Soc.*, **42**, 239 (1920); Sutherland, *Phil. Mag.*, **3**, 161 (1902); **12**, 1 (1906); **14**, 3 (1907); Milner, *Phil. Mag.*, **35**, 214, 354 (1918); *Trans. Faraday Soc.*, **15**, 148 (1919); Ghosh, *J. Chem. Soc. London*, **113**, 449 (1918); *Trans. Faraday Soc.*, **15**, 154 (1919); Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

[2] See the summary by Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

[3] Schlesinger and his students, *J. Am. Chem. Soc.*, **41**, 1,923 (1919).

TABLE 76.—CONDUCTIVITIES IN ANHYDROUS FORMIC ACID AT 25°

Potassium Formate

Mols per liter of solution	Specific conductance	Equivalent conductance	Ionization in solution
0.000	....	(68.92)	1.000
0.1027	0.006516	63.43	0.920
0.1314	0.008167	62.18	0.902
0.1992	0.01187	59.55	0.864
0.2433	0.01411	57.99	0.841
0.3104	0.01738	55.99	0.812
0.3266	0.01812	55.48	0.085

Sodium Formate

Mols per liter of solution	Specific conductance	Equivalent conductance	Ionization in solution
0.000	....	(66.22)	....
0.06418	0.003960	61.70	0.932
0.09682	0.005786	59.75	0.902
0.1755	0.009820	55.94	0.845
0.2337	0.01256	53.72	0.811
0.2734	0.01429	52.28	0.789
0.2954	0.01522	51.54	0.778
0.3153	0.01606	50.94	0.769

Lithium Formate

Mols per liter of solution	Specific conductance	Equivalent conductance	Ionization in solution
0.0000	....	(64.72)	....
0.0671	0.003917	58.38	0.902
0.1018	0.005689	55.86	0.863
0.1524	0.008061	52.90	0.817
0.2044	0.01030	50.38	0.778
0.2480	0.01203	48.51	0.750
0.3076	0.01423	46.24	0.714

Solutions of sodium iodide in acetone[1] and in isoamyl alcohol[2] also conduct electricity in much the same way as aqueous solutions; a limiting equivalent conductance is approached at small concentrations, and from the ratio of this limiting value to the equivalent conductance at other concentrations, a fractional ionization of sodium iodide is calculated which is of the same order as that in water solutions. Table 77 shows the results of experiments.

TABLE 77.—CONDUCTIVITY OF SODIUM IODIDE IN ACETONE AND ISOAMYL ALCOHOL

Equivalent concentration	Equivalent conductivity in acetone			Equivalent conductivity in isoamyl alcohol at 25°
	0°	25°	40°	
1.0000	....	26.4	28.65	
0.5000	32.5	38.4	41.00	1.396
0.2000	44.9	52.7	56.60	1.339
0.1000	53.7	64.1	68.90	1.294
0.0500	63.1	76.1	82.70	....
0.0200	77.2	95.0	103.80	1.649
0.0100	89.0	109.7	121.40	2.024
0.0050	99.0	124.5	139.40	2.560
0.0020	111.0	143.2	163.00	3.394
0.0010	118.5	155.0	178.00	4.184
0.0005	125.0	164.6	188.90	....
0.0002	129.4	171.7	197.20	6.115
0.0001	129.9	173.6	199.90	6.636
0.0000	(131.4)	(176.2)	(204.00)	(7.790)

Conductvity of Pure Liquids.—The conductivity of water and of other pure liquids at ordinary temperatures is very slight, but has been shown in the case of water to be due to a real ionization, and not to any contained impurities. The conductivity of liquids increases with the temperature, quite rapidly in the case of water, but usually does not reach a point where the liquids are good conductors of electricity.

Fused salts are, on the other hand, very good conductors of electricity. Their conductivity is undoubtedly due to ions, just as that of their aqueous solutions is due to ions; the products of electrolysis are often the same as the products of electrolysis of their water solutions, except in cases where these would react with water. Fused lead chloride yields upon electrolysis lead at the cathode and chlorine at the anode; the same products result when aqueous solutions of it are electrolyzed.

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[1] McBain and Coleman, *Trans. Faraday Soc.*, **15**, 27 (1919).

[2] Keyes and Winninghoff, *Proc. Nat. Acad. Sci.*, **2**, 342 (1916).

Fused sodium hydroxide yields metallic sodium at the cathode and oxygen at the anode when it is electrolyzed; this same effect is produced by electrolysis of sodium hydroxide solution with a mercury cathode in which sodium can dissolve and be protected from the action of water;[1] Faraday's law describes quantitatively the yield in both cases. But owing to the fact that salts in the fused condition are acting as both solvent and solute, ionic velocities have not yet been determined, and transference experiments are impossible, as appreciable concentration changes do not occur around the electrodes.

The industrial importance of electrolysis of fused salts is very great. Metallic sodium is produced almost entirely by electrolysis of fused sodium hydroxide; magnesium metal from the electrolysis of fused magnesium chloride; aluminum from the electrolysis of a solution of aluminum oxide in fused cryolite, a fluoride of sodium and aluminum. Some attempts have been made to develop the theory of fused salts,[2] but an adequate treatment of them has not yet been accomplished.

Questions

(Numerical data for solving problems should be sought in the tables given in the chapter.)

1. State briefly the fundamental assumptions of the ionic theory. What facts have supported each of them?

2. Summarize the facts which have led to the hypothesis that salts are completely ionized in solution.

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[1] When sodium hydroxide solution is electrolyzed with a platinum cathode, sodium does not deposit and then react with water to produce sodium hydroxide and hydrogen, as is sometimes stated. Hydrogen is evolved at the cathode and oxygen at the anode during this electrolysis, when the applied electrical potential is insufficient to cause the deposition of sodium. Metallic sodium is deposited in a mercury cathode as an amalgam only upon application of a much higher potential than is required to discharge hydrogen at a platinum electrode.

[2] Goodwin and Wentworth, *Phys. Rev.*, **24**, 77 (1907); **25**, 469 (1907).

3. A solution 0.1 formal in nitric acid freezes at − 0.35°. Calculate the fraction of it which is ionized. From this result, and the limiting conductances of its ions, calculate the specific resistance of the solution at 25°.

4. What weight of copper would be deposited by a current of 10 amperes flowing through copper sulfate solution for 24 hours.? How long would it take to deposit a ton of copper if a current of 2,000 amperes was used? A ton is 906 kilos.

5. It is desired to plate a square foot of sheet iron with a layer of copper 0.1 mm. thick in 12 hours. What current will be required? The density of copper is 8.95; both sides of the sheet are to be covered.

6. How long would a current of 1 ampere flow in order to liberate a gram of iodine, atomic weight 126.9? What weight of silver (atomic weight 107.88) would be deposited by the same quantity of electricity?

7. Calculate the specific resistance at 0°C. of a one per cent solution of sodium chloride. Calculate the same resistance at 100°.

8. In a rectangular trough 20 cm. long provided with a copper electrode at each end, are poured 100 c.c. of 0.1 normal $CuSO_4$ solution. With 100 volts at the electrodes what is the resultant current?

9. A current of 50 milliamperes is passed for 5 hours through a dilute solution of sodium bromide between silver electrodes coated with silver bromide. Describe quantitatively the changes that occur in each electrode portion in accordance with Faraday's law and with the law of transference. Make also a quantitative statement of the net effect of these changes in each portion. The equivalent conductances are Na = 43.4; Br = 67.7; silver bromide forms at the anode, and silver bromide is reduced to metallic silver at the cathode.

10. A sample of "hard water" known to contain only calcium sulfate and calcium bicarbonate in appreciable quantities is submitted for analysis. At 18° the specific conductivity of the hard water is 0.00100. It is boiled (without loss of water) and cooled to 18°, when its specific conductivity is found to be 0.000757. Assuming that each salt is 85 per cent ionized and that boiling completely changes the calcium bicarbonate to insoluble $CaCO_3$, calculate the concentration of calcium sulfate ("permanent hardness") and of calcium bicarbonate ("temporary hardness"), expressing the results as formula weights per liter. The equivalent conductances are Ca = 52, SO_4 = 68.5, HCO_3 = about 35.

11. A 0.1 normal solution of NaCl has at 18° a specific resistance of 108.7 ohms, and is 84.5 per cent ionized. In a given transference experiment this solution is electrolyzed between a silver anode and a silver cathode coated with silver chloride; the anode is found to gain in weight by 0.177 gram, and the cathode portion to increase its content in sodium chloride by 0.117 gram. (*a*) Calculate the equivalent conductance of the sodium-ion at 18°. (*b*) Calculate the rate, expressed in centimeters per hour, at which the chloride ion would migrate through the solution at 18° under a potential gradient of 2 volts per centimeter.

12. (*a*) Calculate the specific conductance at 18° of 0.05 formal $BaCl_2$, assuming it is 12 per cent ionized into $BaCl^+$ and Cl^-, and 65 per cent ionized

into Ba^{++} and Cl^-. (*b*) Calculate the freezing point of the solution. Assume the equivalent conductance of the intermediate ion $BaCl^+$ to be 25.

13. Calculate the values of $1/\Lambda$ and of $(C\Lambda)^{1/2}$ for each concentration of silver nitrate given in Table 67. Make a plot of these values, and by drawing the best straight line through the points determine the value of the intercept of the line on the axis $C\Lambda = 0$. From this intercept, calculate a value for the limiting equivalent conductance of silver nitrate.

14. Plot the values of the equivalent conductivity of sodium formate in anhydrous formic acid against the concentration, draw a smooth curve through the points and extend this curve to the axis corresponding to zero concentration to determine the limiting equivalent conductance.

15. A dilute solution of nitric acid is electrolyzed between platinum electrodes. Predict the net changes, expressed in equivalents of acid, resulting in each electrode portion per faraday of electricity passed through the solution. Hydrogen ion moves five times as fast as nitrate ion, and the anode process consists in the evolution of oxygen gas.

CHAPTER VII

THERMOCHEMISTRY

The heat effect of a chemical change has attracted the attention of chemists almost from the beginning of exact work in chemistry. It was thought for a long time that the heat evolved during a chemical reaction was a measure of the chemical affinity of the substances combining, since those reactions which proceed with the evolution of large quantities of heat (such as the combustion of carbon or of hydrogen) result in the formation of very stable molecules. That the "chemical affinity," or driving force of a reaction could not be measured in this way was realized after the discovery of reactions which proceeded of themselves, but with the *absorption* of heat from the surroundings. The problems of thermochemistry did not become on that account less interesting or of less importance; indeed they led the way to the discovery of the true relation between chemical driving force and reaction heat. Heats of reaction are of great importance in calculating chemical equilibrium at one temperature from the experimental data at another temperature, and in many other ways which will appear later in their proper place.

Thermochemical Methods.—A reaction whose heat effect is desired is carried out in a suitable vessel immersed in a tank of water, which must be protected from losses of heat to its surroundings. The rise in temperature of this tank (called the calorimeter) is determined by a sensitive thermometer, and from this rise and the known heat capacity of the calorimeter is calculated the heat effect. In order to remove any danger of heat exchange between the calorimeter and its surroundings, these are often maintained at the same temperature as the calorimeter itself. As the temperature of the latter rises during a reaction produced in it, a parallel rise is produced in the surroundings, usually by adding sulfuric acid to a solution of sodium hydroxide, or by electric heating. A diagram of such a piece of apparatus is

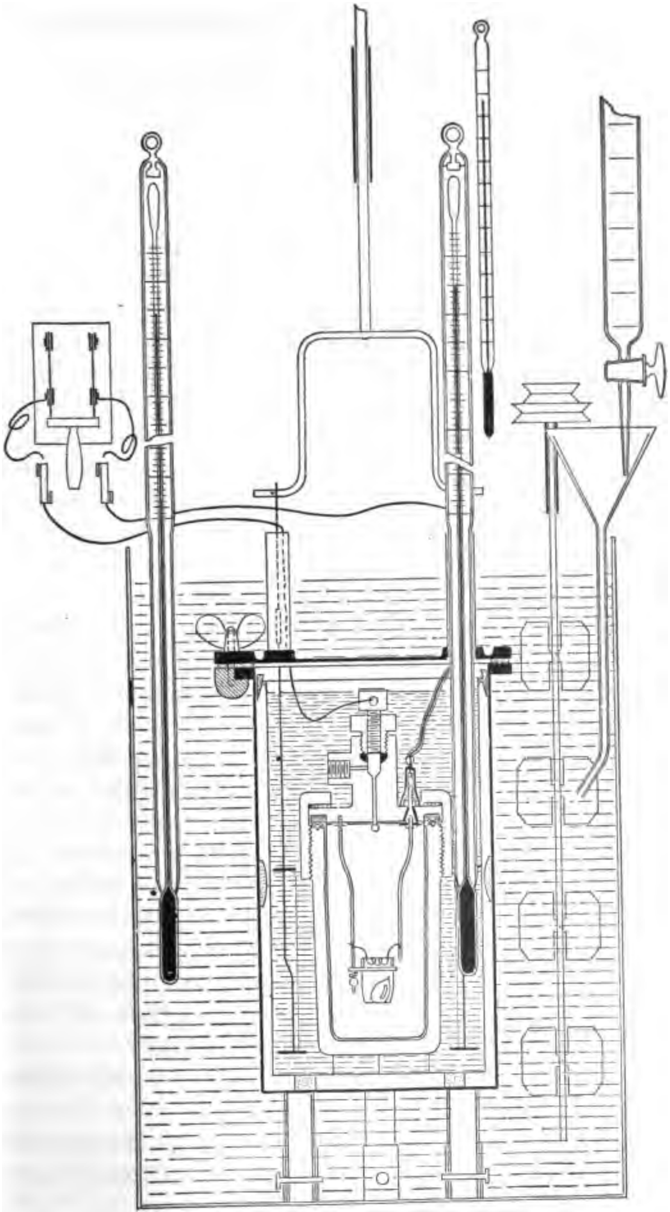

FIG. 35.—Submerged calorimeter, arranged for combustion of a volatile liquid.

shown[1] in Fig. 35, which shows the bomb type of calorimeter arranged for burning a volatile liquid.

The material to be burned is placed in a glass receptacle of very thin walls in a platinum crucible suspended in a heavy steel bomb, lined with gold to prevent any chemical action taking place upon it. The lid is screwed on the bomb, it is filled with oxygen under considerable pressure, and the bomb is closed by the screw valve at its top. The bomb is then placed in the calorimeter (the inner vessel of water) and this is put in another vessel slightly larger than the calorimeter, and closed by a water tight cover having two outlet tubes for a thermometer and the stirring mechanism. All of this apparatus is submerged in a large tank of sodium hydroxide solution in which is an efficient stirrer and another thermometer, shown at the left. The inner vessel is stirred by a perforated disc moved up and down by the Y-shaped rods shown at the top of the diagram; and the outer bath is stirred by paddles shown at the right until the whole system is at the same temperature.

Upon closing the electric switch, the tiny iron wire shown at the top of the platinum crucible is burned out, its molten products fall on the glass bulb and break it, thus igniting its contents and burning them completely by means of the excess oxygen present. The heat evolved causes a rise in temperature which is indicated on the thermometer reaching to the inner vessel; and a parallel rise in temperature of the outside vessel is produced by adding strong sulfuric acid from a buret at the required rate. Since the outer bath is always kept at the same temperature as the calorimeter within it, there is no exchange of heat between them, and all of the heat of reaction is used to raise the temperature of the calorimeter itself. There is thus no heat-loss correction to be made, and the total heat effect is the product of temperature rise and heat capacity of the calorimeter. From preliminary experiments, the heat capacity of the calorimeter bomb is determined, and it is immersed in a measured quantity of water. Thus all the data needed for computing the heat effect are at hand, and since a weighed quantity of substance was burned, the heat evolution per formula weight is readily computed.

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[1] The author is indebted to Prof. T. W. Richards of Harvard College for this diagram of his latest type of submerged calorimeter.

Heat effects of reactions taking place in solutions may be determined in the same way, substituting for the bomb a thin platinum vessel containing one solution. The other solution is discharged into this vessel from a pipet immersed in the calorimeter, in order that the solutions may be at the same temperature when they are mixed for the reaction.

First Law of Heat.—This law is also called the first law of thermodynamics, or the law of conservation of energy. It states that energy cannot be created or destroyed, but only changed from one form into another, and that the conversion of one kind of energy into another always proceeds without loss in the total energy. It follows from this law that the energy evolved by a system on changing from one state to another is independent of the manner in which this change is brought about, so long as the same final state is reached from the given initial state. For if the energy evolved by one path was less than by another, the change in state could be brought about by the process evolving the greatest energy, reversed by a path involving less energy, and an excess of energy would have been created, which is contrary to the law as stated.

It also follows from this law that the energy evolved in a chemical change is absorbed when the change is reversed, for if this were not true a given change could be reversed with less energy than that given up by the first change, and energy would have been created in the cycle. The heat absorbed by any substance when it is heated is evolved completely when this substance is cooled to the original temperature. Another way of stating this fact is that the energy content of a system (any combination of matter) depends only on the conditions under which it exists. We have no way of determining the total quantity of energy in any system, but only changes in the energy content of it. But if all of the energy added to a system undergoing a certain change is evolved when that change is reversed, it is established that the energy within the system is the same as it was before the change took place.

Changes in the State of a System.—To define the state of a system we must describe the quantity and composition of it, the state of aggregation (gas, liquid or solid) of each of its parts if it is not homogeneous, and give the temperature and pressure.

Thus a certain system consists of a mol (342 grams) of sugar and 12 mols (384 grams) of oxygen at 20° and 1 atmosphere pressure. By combustion this system may be changed into 12 mols (528 grams) of carbon dioxide and 11 mols (198 grams) of liquid water at 20° and 1 atmosphere pressure, and a certain quantity of heat will be evolved. It is not necessary that the system remain at 20° during the change, but only that it be brought to 20° when the change is completed. By combustion the system would be raised to a higher temperature, and it would be necessary to take heat away from the system in order to restore the original temperature. The quantity of heat taken away in order to restore the original temperature is 1,349,400 cal.; and this represents the loss in energy content for the system. The system composed of carbon dioxide and water is poorer in energy than the system composed of sugar and oxygen by this quantity of energy. This is called the heat of the reaction, or sometimes the decrease in heat content of the system attending the change in state. The two terms are of course identical in meaning.

Heat Capacities and Specific Heats.—One of the simplest changes in state is that which occurs when a homogeneous substance is heated. We have already considered this type of change under the specific heats of the various substances. When a monatomic gas is heated, the energy absorbed per degree at constant pressure is 5.0 cal. per mol (Chapter III); the absorption of heat per degree for diatomic gases is somewhat larger, and increases with the temperature. Thus for HCl, HBr, HI, O_2, N_2, H_2, CO and NO the molal heat capacity is $6.5 + 0.001T$, the heat absorbed per mol is the integral of $(6.5 + 0.001T)dT$ between the absolute temperatures involved. The molal heat capacity of halogens in the vapor state is larger, and changes with the temperature more rapidly than that of the other diatomic gases; it is given by the expression $(6.5 + 0.004T)$. The integral of this expression between the desired limits gives the heat absorbed when the halogens are heated in the form of vapor at constant pressure.

For more complex molecules the change of heat capacity with the temperature is not uniform, and quadratic or cubic equations must be used to express the results of experiment over a range of temperature. For water vapor and hydrogen sulfide the equation representing molecular heat capacity is[1]

$$C_p = 8.81 - 0.0019T + 0.00000222T^2; \qquad (1)$$

for carbon dioxide and sulfur dioxide it is

$$C_p = 7.0 + 0\ 0071T - 0.00000186T^2; \qquad (2)$$

and for ammonia gas

$$C_p = 7.5 + 0.0042T; \qquad (3)$$

where T denotes the absolute temperature. To illustrate the use of these equations, let us calculate the heat required to raise a mol of steam from 100° to 150°C.

$$\text{Heat absorbed} = \int_{373}^{423} (8.81 - 0.0019T + 0.00000222T^2)\ dT$$

$$= \left[8.81\ (423 - 373) - \frac{0.0019}{2}\left(\overline{423}^2 - \overline{373}^2\right) + \frac{0.00000222}{3}\left(\overline{423}^3 - \overline{373}^3\right)\right] = 440.5 - 38 + 18$$

or 420 cal. It should be remembered that the heat capacity is a temperature function; and that the heat absorbed is an integral of $C_p\ dT$ between the temperature limits involved.

These data are all for constant pressure; that is, they include the heat expended in forcing back the atmosphere. As this is R calories per degree for ideal gases, the molal heat capacities of gases at constant volume are approximately 2 cal. per degree less than those at constant pressure. Thus, $(4.5 + 0.004T)$ for chlorine at constant volume, $(5.0 + 0.0071T - 0.00000186T^2)$ for carbon dioxide at constant volume.

No simple expressions are known for the heat capacities of liquids; they are generally slightly larger than those for the corresponding solids.

The heat capacities of most of the solid elements approach about 6.2 cal. per atomic weight near room temperature; they fall off rapidly at lower temperatures in a way which is not expressible by a simple equation such as that used for gases. Above ordinary temperature the atomic heats of most solids increase only slightly as higher temperatures are reached.

The heat capacities of solid compounds are roughly equal to the sum of the heat capacities of the elements in them (Kopp's law). Thus the molecular heat capacity of lead iodide is about equal to that of an atomic weight of lead plus that of two atomic weights of iodine, or about 18.6 cal. per formula weight. When solids are formed from elements which are gases at room temperatures, or from the lighter elements which do not conform to Dulong and Petit's law, their molecular heat capacities are somewhat less than those of the compounds formed from heavy elements. But since the difference between the heat capacity of copper and copper oxide is about the same as that between zinc and zinc oxide or lead and lead oxide, it is possible to assign to gaseous elements a figure which represents the heat capacity of them in their solid compounds. These figures are given on page 96.

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[1] Lewis and Randall, *J. Am. Chem. Soc.*, **34**, 1,128 (1912).

Changes in State of Aggregation.—Heats of evaporation have already been considered under Trouton's law (Chapter III). The heat absorbed in small calories per mol of liquid evaporated is approximately 20.3 times the absolute boiling point. Large deviations from this rule are often found, and recourse to experiment is necessary when reliable data are required.

The heat of fusion is a quantity for which no general rule similar to Trouton's rule is known.

Thermochemical Equations.—It is convenient to represent the data of thermochemistry by ordinary chemical equations, to which are added terms indicating the heat effects observed. As an example we may take the combustion of sugar mentioned above. This may be expressed, for 20°,

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O(\text{liq.}) + 1{,}349{,}400 \text{ cal.}$$

In these equations, the formula for a substance represents a formula weight of it just as it does in an ordinary chemical equation, the positive sign of the heat effect indicates that heat is evolved. Similarly

$$H_2O(\text{liq.}) = H_2O\ (\text{gas}) - 9{,}700 \text{ cal. at } 100°$$

indicates the absorption of 9,700 cal. of heat from the surroundings during the vaporization of a formula weight of water at 100°.

One other point should be made clear; that the thermochemical equation represents a completed reaction. Thus the equation

$$H_2 + I_2\ (\text{gas}) = 2HI + 1300 \text{ cal. at } 300°$$

does not state that this quantity of heat will be evolved when a formula weight of hydrogen and one of iodine are brought together at 300°, for the reaction reaches a state of equilibrium, such that no more hydrogen iodide is formed, when there are substantial quantities of both hydrogen and iodine remaining. The equation states that when *two formula weights of hydrogen iodide are formed* at 300°, 1,300 cal. of heat are evolved. The excess of reacting substances remains unchanged and so does not evolve heat. Thus approximately this quantity of heat would be evolved if one formula weight of iodine and a hundred mols of hydrogen were brought together, for then the reaction would be substantially complete.

Law of Constant Heat Summation. (Law of Hess).—This law states that when a reaction is brought about in steps, the sum of the heat quantities evolved in all the steps is equal to that which would have been evolved had the reactions taken place all at once. This law was announced before the conservation of energy was accepted as a universal fact; we now know that it is only a special case of the more general law of the conservation of energy. It is very useful in calculating the heat effect for reactions which do not take place readily and quickly. Since the data of thermochemistry are obtained by the use of a calorimeter, it is clear that exact determinations cannot be made if the reaction proceeds slowly for several hours, for the radiation losses from the calorimeter would lead to uncertainty in the measured heat quantity.[1] Many reactions take place in one direction only. The law of conservation of energy states that if the reaction is reversed, the heat which was absorbed in the first case will be evolved in the second. Thus from the reaction

$$H_2 + {}^1/_2O_2 = H_2O(\text{liq.}) + 68{,}400 \text{ cal. at } 20^\circ$$

we are assured that the reverse reaction would absorb this quantity of heat from the surroundings, even though we are unable to reverse it at 20° and determine the heat quantity directly.

Copper oxide will react with hydrogen to form water. If a mol of hydrogen is passed over hot copper oxide (the reaction proceeds too slowly for measurement at room temperature), the quantity of heat evolved will be less than the heat of formation of water from hydrogen and oxygen by the amount of energy necessary to separate the oxygen from copper oxide.

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[1] Barry, *J. Am. Chem. Soc.*, **42**, 1295, 1921 (1920) has developed a calorimeter well suited to measuring heats of slow reactions, but the quantity of data so far obtained is very slight.

Let us consider another indirect process involving two formula weights of hydrogen chloride dissolved in 16 Aq (16 formula weights of water), an atomic weight of iron, and 384 mols of water.[1] First dissolve the iron in strong acid,

$$\mathrm{Fe} + 2(\mathrm{HCl}.8Aq) = \mathrm{FeCl_2}.16Aq + \mathrm{H_2} + 20{,}550 \text{ cal.}$$

Then add water to the solution,

$$\mathrm{FeCl_2}.16Aq + 384Aq = \mathrm{FeCl_2}.400Aq + x \text{ cal.}$$

This same process may be carried out by first adding water to the strong acid, then dissolving the iron in diluted acid. The thermochemical equations are

$$2(\mathrm{HCl}.8Aq) + 384Aq = 2\,(\mathrm{HCl}.200\,Aq) + 2{,}660 \text{ cal.}$$
$$\mathrm{Fe} + 2(\mathrm{HCl}.200\,Aq) = \mathrm{FeCl_2}.400\,Aq + \mathrm{H_2} + 20{,}800 \text{ cal.}$$

The same total change in state has been brought about, for at first we had iron, strong acid, and water, and in the final system we have hydrogen and dilute ferrous chloride. According to the law of conservation of energy, the same total energy change is involved, and hence we may calculate the heat of dilution of ferrous chloride, x, since

$$20{,}550 + x = 2{,}660 + 20{,}800,$$

whence $x = 2{,}910$ cal.

Heats of Combustion.—The heats of combustion of large numbers of organic compounds have been determined carefully, and they are used for another purpose which is explained in the next paragraph. Many organic substances do not burn readily in air; others (such as naphthalene) are not completely changed to water and carbon dioxide when burned in air. It is therefore customary to determine these heats of combustion in a closed calorimeter with oxygen under considerable pressure. Data for almost all of the common organic compounds may be found in Landolt-Börnstein's tables, or in the translation of Thomsen's

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[1] Richards, Rowe and Burgess, *J. Am. Chem. Soc.*, **32**, 1,176 (1910).

Thermochemistry. Many of these heats of combustion were determined before the highest calorimetric precision had been developed, and the data are often in error by one or two per cent. For approximate calculations, this is not serious; but it is a great disadvantage when accurate data are desired. This work is therefore being given careful scrutiny by modern chemists, much of it has been repeated under more favorable conditions, and accurate heats of combustion are rapidly becoming available. Table 78 shows some recently determined heats of combustion which are especially accurate.

TABLE 78.—HEATS OF COMBUSTION AT CONSTANT VOLUME

Substance	Heat of combustion per	
	Gram	Formula weight
Sugar	3,945	1,349,400
Benzoic acid	6,325	771,550
Naphthalene	9,624	1,231,600
Benzene	10,026	781,850
Toluene	10,167	935,230
$C_6H_5C_2H_5$	10,273	1,089,000
ter-Butyl benzene	10,446	1,399,800
Xylene (*o* and *m*)	10,277	1,089,000
Cyclohexanol ($C_6H_{11}OH$)	8,892	889,300
Di-isoamyl	11,356	1,612,600
Methyl alcohol	5,333	170,610
Ethyl alcohol	7,110	327,040
Propyl alcohol	8,044	485,800
Butyl alcohol	8,626	638,330
Isobutyl alcohol	8,610	637,144

Richard and Davis, *J. Am. Chem. Soc.*, **42**, 1,614 (1920); *cf.* **37**, 993 (1915). For other data, see Swietoslawski, *J. Am. Chem. Soc.*, **42**, 1,092 (1920).

Calculation of Heats of Combustion.—The mechanism of combustion of hydrocarbon compounds consists in severing bonds between carbon and carbon, or between carbon and hydrogen, and in establishing unions between carbon and oxygen, and between hydrogen and oxygen. Several simple relations between the heat of combustion and the number and character of bonds severed have been discovered. For example, the formal heat of combustion of a saturated hydrocarbon[1] is approximately 52,700 cal. for each atomic weight of oxygen required to burn it. Ethane requires seven atomic weights of oxygen per mol of it burned; its heat of combustion should therefore be 7 × 52,700 or 368,900 cal., and this is in agreement with experiment. In Table 79 are given the heats of combustion determined experimentally for several compounds, and in the last column the heat of combustion divided by the number of atomic weights of oxygen used.

TABLE 79.—HEAT OF COMBUSTION

Compound	Molal heat of combustion	Heat evolved per atomic weight of oxygen
Methane	210,800	52,700
Ethane	369,000	52,700
Propane	527,500	52,700
Trimethylmethane	685,200	52,700
Tetramethylmethane	844,800	52,800
Di-isopropyl	996,600	52,500

This rule applies only to saturated hydrocarbons. A more general one[2] is stated in terms of the number and character of the bonds severed during combustion. Expressed in thousands of calories, the molal heat of combustion is 52.7 times the number of C—H bonds, plus 52.9 times the number of C—C bonds,[3] plus 121.8 times the number of C=C, plus 203.2 times the number of C≡C bonds, plus 15.0 times the number of C—O bonds. Since the bond C=O is unchanged by combustion, no heat is evolved on account of it. The reliability of this rule is illustrated by Table 80.

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[1] Thornton, *Phil. Mag.*, **33,** 196 (1917).

[2] Redgrove, *Chem. News,* **116,** 37 (1917).

[3] Swietoslawski, *J. Am. Chem. Soc.*, **42,** 1,312 (1920), gives 53.72 for a C—C bond and 52.25 for each C—H. Thus the increase in molal heat of combustion in ascending any homologous seris is two C—H bonds plus one C—C, or 157.8 large calories; Richards, *J. Am. Chem. Soc.*, **42,** 1,616 (1920), gives 153.5 large calories for the average difference in heat corresponding to each CH_2 group added.

TABLE 80.—HEATS OF COMBUSTION

Compound	Bonds severed	Calculated heat of combustion	Measured heat of combustion	Per cent error in calculated value
Ethylene	4C—H + 1C=C	332,600	332,100	0.2
Methyl formate	4C—H + 2C—O	240,800	240,600	0.1
Acetic anhydride	6C—H + 2C—C + 1C—O	452,000	459,500	1.6
Ether	10C—H, 2C—C 2C—O	662,800	657,900	0.8
Methyl acetate	6C—H, 1C—C, 2C—O	399,100	398,400	0.5
Methyl isobutyrate	10C—H, 3C—C, 2C—O	715,700	715,500	0.0
Acetylene	2C—H, C≡C	308,600	313,000	1.4

The agreement leaves something to be desired, but in case no data are available, rough values calculated from these rules will often be of considerable service.

Heats of Reaction at Constant Pressure and at Constant Volume.—Two methods of procedure are followed in calorimetric work, and it is convenient to correct the values obtained by one procedure to those which would have been obtained had the other procedure been employed. Thus when iron is dissolved in acid in an open vessel, the hydrogen formed must force back the atmosphere to make room for itself, thereby doing work. If the reaction had been carried out in a strong closed bomb, a pressure of hydrogen would have been built up and more heat would have been evolved. Later when the bomb is opened, hydrogen rushes out, driving back the atmosphere as it does so, and performs work (at the same time absorbing some of the heat originally given to the surroundings) so that the total heat evolved is the same as during the constant pressure process. The work done is $p(v_2 - v_1)$ in the first process where hydrogen was evolved at 1 atmosphere, and is zero for the constant volume process, as the work done when the bomb is opened is not considered part of the calorimetric process. An amount of heat equivalent to this work done in the constant pressure process is evolved by the constant volume process. We have then, denoting by Q the heat of the reaction,

$$Q_p = Q_v - p(v_2 - v_1). \tag{4}$$

In this expression v_2 is the volume of a mol of hydrogen plus that of a mol of dissolved ferrous chloride, and v_1 is the volume of the iron and acid from which it was formed. There is only a very slight change in the volume of the solution, and the volume of the iron may be neglected in comparison with that of the gas. The work term then becomes practically pv_2, which from the ideal gas equation is RT. Since the value of R is 1.99 cal., the correction term is at once available in calories, and the difference at 20° is $1.99 \times 293 = 586$ cal. per mol of gas generated. This should be rounded to 600 cal., since otherwise upon subtraction we would write down a larger number of significant figures than the experimental work justifies.

For reactions involving only solids and liquids the difference between heats of reaction at constant volume and at constant pressure need not be taken into account. For reactions in which gases are involved the increase in volume is the *increase* in the number of *mols of gas* during the reaction. In general

$$Q_p = Q_v - \Delta nRT \tag{5}$$

where Δn is the *increase in the number of mols of gas* present when the reaction occurs. For the combustion of carbon monoxide, $2CO + O_2 = 2CO_2 + 136{,}000$ cal., Δn is -1, and the heat of combustion of two mols in a closed vessel would be less than in the open air by the amount RT, or 600 cal

All of the data given in this chapter are for a constant pressure of 1 atmosphere, unless otherwise stated. This is generally understood to be the case unless a constant volume process is specifically mentioned.

Heats of Formation.—By means of the law that the total energy change associated with a change in the state of a system is independent of the manner in which this change is brought about, we are able to compute the heats of formation of compounds from their elements, even in cases where this direct synthesis is not possible in the calorimeter. For example, let us write the equation for the formation of benzoic acid from its elements, and a second equation for the complete combustion of benzoic acid into carbon dioxide and water.

$$\begin{array}{rcl} 7C + 3H_2 + O_2 &=& C_6H_5COOH + x \text{ cal.} \\ C_6H_5COOH + 7\frac{1}{2}O_2 &=& 7CO_2 + 3H_2O \text{ (liquid)} + 770{,}000 \text{ cal.} \\ \hline 7C + 3H_2 + 8\frac{1}{2}O_2 &=& 7CO_2 + 3H_2O\text{(liquid)} + 881{,}400 \end{array}$$

Under these reactions is written the sum of them, which is the combustion of carbon and hydrogen. The heat of this last reaction was calculated from the equations

$$\begin{aligned} C + O_2 &= CO_2 + 96{,}600 \text{ cal., and} \\ H_2 + \tfrac{1}{2}O_2 &= H_2O \text{ (liquid)} + 68{,}400 \text{ cal.,} \end{aligned}$$

by multiplying the first one by seven and the second one by three, and adding, which gives the 881,400. The formation of benzoic acid plus its combustion evolves the same amount of heat as the direct combustion of the elements, whence $x + 770{,}000 = 881{,}400$, or

$$7C + 3H_2 + O_2 = C_6H_5COOH + 111{,}400 \text{ cal.}$$

In many cases this indirect method is not needed, as the elements combine directly and readily in the calorimeter. Some examples are quoted for reference, and as data for use in solving the problems at the end of the chapter.

TABLE 81.—HEATS OF FORMATION OF CHEMICAL COMPOUNDS[1]

$$\begin{aligned} Pb + I_2 &= PbI_2 + 41{,}850 \text{ cal.} \\ Ag + I &= AgI + 15{,}100 \text{ cal.} \\ Pb + Cl_2 \text{ (gas)} &= PbCl_2 + 85{,}700 \text{ cal.} \\ Pb + Br_2 \text{ (liq.)} &= PbBr_2 + 66{,}350 \text{ cal.} \\ Ag + \tfrac{1}{2}\, Cl_2 \text{ (gas)} &= AgCl + 30{,}410 \text{ cal.} \\ 2Na + S &= Na_2S + 89{,}700 \text{ cal.} \\ Na_2S + Aq &= Na_2S \text{ (dissolved)} + 15{,}500 \text{ cal.} \\ 2K + S &= K_2S + 87{,}100 \text{ cal.} \\ K_2S + Aq &= K_2S \text{ (dissolved)} + 22{,}700 \text{ cal.} \\ H_2 + Cl_2 &= 2HCl \text{ (gas)} + 44{,}000 \text{ cal.} \\ HCl \text{ (gas)} + 200\, Aq &= HCl.200Aq + 17{,}300 \text{ cal.} \\ Na + \tfrac{1}{2}Cl_2 &= NaCl + 97{,}900 \text{ cal.} \\ H_2 + S &= H_2S + 2{,}730 \text{ cal.} \end{aligned}$$

[1] Partly from Braune and Koref, *Z. anorg. Chem.*, **87**, 175 (1914).

TABLE 81.—(*Continued*)

$$\left.\begin{array}{rcl} K + \frac{1}{2}\,Br_2\ (\text{liquid}) & = & KBr + 95{,}310\ \text{cal.} \\ \frac{1}{2}\,Br_2\ (\text{gas}) & = & \frac{1}{2}\,Br_2\ (\text{liquid}) + 3{,}750\ \text{cal.} \\ \hline K + \frac{1}{2}\,Br_2\ (\text{gas}) & = & KBr + 99{,}060\ \text{cal.} \end{array}\right\}$$

$$\left.\begin{array}{rcl} K + \frac{1}{2}\,I_2\ (\text{solid}) & = & KI + 80{,}130\ \text{cal.} \\ \frac{1}{2}\,I_2\ (\text{gas}) & = & \frac{1}{2}\,I_2\ (\text{solid}) + 7{,}400\ \text{cal.} \\ \hline K + \frac{1}{2}\,I_2\ (\text{gas}) & = & KI + 87{,}530\ \text{cal.} \end{array}\right\}$$

$$K + \tfrac{1}{2}\,Cl_2\ (\text{gas}) = KCl + 105{,}610\ \text{cal.}$$

$$\begin{array}{rcl} Ca + \frac{1}{2}\,O_2 & = & CaO + 151{,}400\ \text{cal.} \\ Sr + \frac{1}{2}\,O_2 & = & SrO + 139{,}400\ \text{cal.} \\ Ba + \frac{1}{2}\,O_2 & = & BaO + 126{,}400\ \text{cal.} \end{array}$$

Certain regularities in heats of formation have been pointed out[1] in connection with the groups in the periodic table, of which examples are quoted above. The molal heat of formation of strontium oxide is very nearly the average of the molal heats of formation of calcium oxide and barium oxide. Similarly the molal heats of formation of bromides are about the average of the heats of formation of corresponding chlorides and iodides, after due allowance has been made for the fact that bromine is a liquid and iodine is a solid. For example, the heat of formation of calcium iodide from calcium and iodine vapor is the sum of the equations

$$\begin{array}{rcl} Ca + I_2\ (\text{solid}) & = & CaI_2 + 127{,}400\ \text{cal.} \\ I_2\ (\text{gas}) & = & I_2\ (\text{solid}) + 14{,}800\ \text{cal.} \\ \hline Ca + I_2\ (\text{gas}) & = & CaI_2 + 142{,}200 \end{array}$$

The heat evolution when a mol of calcium chloride forms is 190,400 cal., and the average of these heats should be about the heat of formation of calcium bromide from calcium metal and bromine vapor. This average is 166,300 cal., the experimental value is

$$\begin{array}{rcl} Ca + Br_2\ (\text{liquid}) & = & CaBr_2 + 154{,}200\ \text{cal.} \\ Br_2\ (\text{gas}) & = & Br_2\ (\text{liquid}) + 7{,}500\ \text{cal.} \\ \hline Ca + Br_2\ (\text{gas}) & = & CaBr_2 + 161{,}700. \end{array}$$

The calculated heat of formation is about 3 per cent in error, which illustrates the general accuracy of this rule of average heats.

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[1] Mixer, *Am. J. Sci.*, **37**, 519 (1914).

Heat Content of Compounds at Constant Pressure.—The reaction $2Na + S = Na_2S + 89{,}700$ cal. shows that the heat content of the compound is less than that of the elements from which it was formed by 89,700 cal. There is no way of determining the total heat content of a substance, but it is customary to consider the heat content of each element as zero and refer compounds to this standard. Then the total heat content of sodium sulfide is −89,700 cal., referred to its elements, since this amount of heat was evolved during its formation. Similarly the heat content of hydrogen chloride is 22,000 cal. less than that of its constituent elements, and the heat content of $HCl.200Aq$ is −37,300 cal., referred to the elements and to the solvent water as zero. If we let the symbol for a substance in a thermochemical equation represent its heat content referred to the elements as of zero heat content, we should have in the above example

$$\begin{aligned} 2Na + S &= Na_2S + 89{,}700 \text{ cal.} \\ 0 + 0 &= -89{,}700 + 89{,}700 \end{aligned}$$

and the equation is seen to balance. This gives a ready means of calculating the heat of a reaction in terms of the heats of formation of the substances involved in it; for in the chemical equation we need only substitute the negative of the heat evolved upon formation for each substance and solve for the remaining term which will cause the equation to balance. For example

$$\begin{aligned} Na_2S + 2HCl \text{ (gas)} &= 2NaCl + H_2S \text{ (gas)} + x \text{ cal.} \\ -89{,}700 + 2(-22{,}000) &= 2(-97{,}900) + (-2{,}730) + x \end{aligned}$$

whence $x = 2{,}730 + 195{,}800 - 44{,}000 - 89{,}700 = 64{,}830$ cal., and the heat evolution of this reaction is 64,830 cal. This same result might have been attained by adding together in appropriate way the thermochemical equations from which the heats of formation were taken, as follows:

$$\begin{aligned} Na_2S &= 2Na + S - 89{,}700 \text{ cal.} \\ 2HCl &= H_2 + Cl_2 - 44{,}000 \text{ cal.} \\ 2Na + Cl_2 &= 2NaCl + 195{,}800 \text{ cal.} \\ H_2 + S &= H_2S + 2{,}730 \text{ cal.} \\ \hline Na_2S + 2HCl &= H_2S + 2NaCl + 64{,}830 \text{ cal.} \end{aligned}$$

Heat of Solution.—Some substances dissolve in water with the absorption of heat (ammonium salts, many potassium compounds) but the majority of solids and liquids, and all gases, evolve heat when they dissolve in water. The heat effect depends on the quantity of water used per mol of dissolved substance up to a certain limit; which limit may be determined by dilution experiments. For example, the solution of one mol of hydrogen chloride in 250 cubic centimeters of water evolves 16,500 cal., the addition of 250 cubic centimeters more water evolves 450 cal., the addition of 500 more (to make a total of one liter) evolves 300 cal. more, the dilution with another liter of water only 150 cal., and further addition of water causes no appreciable heat effect. Hence the solution of one mol of hydrogen chloride in two liters of water evolves as much heat as its solution in a larger quantity of water. Such a solution is written $HCl.Aq$; one containing less water should be written with the number of gram molecules of water indicated, as $HCl.28Aq$ for a two normal solution, $HCl.55Aq$ for a normal solution, etc. As thermochemical equations, the heats of dilution are written

$$HCl.20Aq + 80Aq = HCl.100Aq + 480 \text{ cal.}$$

It has been found upon mixing solutions of salts which are highly ionized that there is practically no heat effect attending the formation of the new salts, provided these do not precipitate from solution. The heat effect of $NaCl.Aq + KNO_3.Aq = KCl.Aq + NaNO_3.Aq$ is very small, but the heat effect of $AgNO_3.Aq + NaCl.Aq = AgCl \text{ (solid)} + NaNO_3.Aq$ is considerable, owing to the formation of a solid substance from constituents existing in solution.

Heat of Neutralization.—The average heat effect when a dilute ionized acid is added to a dilute ionized base is 13,800 cal. per mol of water formed. That is, the heat of reaction between hydrogen ion and hydroxyl ion to form water is 13,800 cal. per mol. The case is quite different with slightly ionized substances such as weak acids and bases; but it is often impossible in calorimetric experiments to dilute these solutions to such concentrations that they are largely ionized. Substantially complete ionization may be brought about in another way however, by removing one of the products of ionization. The reaction

$$NH_4OH = NH_4^+ + OH^-$$

proceeds to completion in the presence of an acid which supplies hydrogen ions to combine with the hydroxyl ions as soon as they are formed, and the net effect as shown by the equations

$$\begin{array}{l} NH_4OH = NH_4^+ + OH^- + x \text{ cal.} \\ H^+ + OH^- = H_2O + 13{,}800 \text{ cal.} \\ \hline NH_4OH + H^+Cl^- = H_2O + NH_4^+Cl^- + 12{,}300 \text{ cal.} \end{array}$$

is readily carried out by mixing ammonium hydroxide with hydrochloric acid in a calorimeter. And since $13{,}800 + x = 12{,}300$, $x = -1{,}500$ cal. Such effects are not observed during neutralization of strong electrolytes as shown by the following reactions.[1]

$$\begin{array}{l} HCl.Aq + KOH.Aq = KCl.Aq + H_2O + 13{,}930 \text{ cal.} \\ HCl.Aq + NaOH.Aq = NaCl.Aq + H_2O + 13{,}680 \text{ cal.} \\ HBr.Aq + NaOH.Aq = NaBr.Aq + H_2O + 13{,}750 \text{ cal.} \\ HI.Aq + NaOH.Aq = NaI.Aq + H_2O + 13{,}680 \text{ cal.} \\ HNO_3.Aq + NaOH.Aq = NaNO_3.Aq + H_2O + 13{,}690 \text{ cal.} \\ HNO_3.Aq + KOH.Aq = KNO_3.Aq + H_2O + 13{,}870 \text{ cal.} \\ HNO_3.Aq + TlOH.Aq = TlNO_3.Aq + H_2O + 13{,}690 \text{ cal.} \end{array}$$

All of these reactions are essentially the union of hydrogen ion with hydroxyl ion, since the negative ion of the acid and the positive ion of the base constitute the ions of the salt formed. The differences are not due to errors of experiment, but the variations are small enough to be overlooked, and we may write as a summary of all these reactions the rounded value

$$H^+ + OH^- = H_2O + 13{,}800 \text{ cal. at } 20°.$$

To be sure, the acids and bases employed are already highly ionized, so that the heat of further ionization would be slight, but the fact that this is not the case with weak bases and acids may be deduced from experiments such as the neutralization of ammonia with a strong acid.

Heat of Neutralization and Temperature.—The average value 13,800 cal. stated above does not apply to other temperatures, as will be seen from the following table.[1]

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[1] Wörmann, *Annalen der Physik,* **18**, 775 (1905).

TABLE 82.—HEAT OF NEUTRALIZATION AT DIFFERENT TEMPERATURES

Temperature	Salt formed by neutralization			
	KCl	NaCl	KNO_3	$NaNO_3$
0	14,740	14,590		
6	14,460	14,350	14,430	14,360
18	13,930	13,680	13,870	13,700
32	13,160	12,960	13,100	12,920

Heat of Reaction and Temperature.—Consider a reaction which may occur at two temperatures T_1 and T_2, and let the heat evolved by the reaction be Q_1 at T_1 and Q_2 at T_2. The reaction may occur at T_1, after which the products of reaction are heated to T_2, or the reacting substances may be heated to T_2 and the reaction allowed to take place at that temperature. The total heat effect in these two steps must be the same, for in each case the initial state of the system consists of the reacting substances at T_1; and its final state consists of the reaction products at the temperature T_2. Let us take as an illustration the combustion of carbon monoxide with oxygen. At 20° this reaction is represented by the thermochemical equation

$$CO + \tfrac{1}{2}O_2 = CO_2 + 68{,}000 \text{ cal.},$$

and it is desired to calculate the heat effect at 200°. The following diagram shows the method of calculation:

$$\begin{tikzcd}
\underset{200^\circ}{CO + \tfrac{1}{2}O_2} \arrow[r, "Q_2"] & \underset{200^\circ}{CO_2} \\
\underset{20^\circ}{CO + \tfrac{1}{2}O_2} \arrow[r, "Q_1"] \arrow[u, "(a)"'] & \underset{20^\circ}{CO_2} \arrow[u, "(b)"']
\end{tikzcd}$$

We shall consider the heat evolved by the system in each of the steps, so that Q_1 is +68,000 cal., (*b*) is a negative heat evolution; (a) is a negative heat evolution, and Q_2 is to be calculated. Since (a) + Q_2 may be considered as one path between the initial state of the system (1 CO and $\frac{1}{2}O_2$ at 20°) and the final state of the system (1 CO_2 at 200°), and Q_1 + (b) another path by which the same change of state occurs,

$$(a) + Q_2 = (b) + Q_1.$$

This is required by the first law of heat, since if it were not true the change of state could be brought about by one path, reversed by the path evolving the smaller quantity of energy, thus restoring the system to its original state, and creating energy without any loss of energy from the system. This is impossible in the light of all experience. Here Q_1 is known, and (a) and (b) may be calculated from specific heat data. For the process (a) we must heat one and a half mols of diatomic gas from 20 to 200°, evolving the quantity of heat

$$(a) = -1.5\int_{293}^{473}(6.5 + 0.001T)\,dT = -1{,}858 \text{ cal.}$$

For (b), one mol of carbon dioxide is heated through the same temperature range.

$$(b) = -\int_{293}^{473}(7.0 + 0.0071T - 0.00000186T^2)dT = -1{,}708 \text{ cal.};$$

We may now calculate the heat effect at the higher temperature.

$$-1{,}858 + Q_2 = -1{,}708 + Q_1;\ Q_2 = +68{,}150$$

Combustion of a mol of carbon monoxide at 200° evolves 68,150 cal. of heat.

The general method of calculating a heat effect at one temperature from the value of it at another temperature is that indicated above. In the expression used, $Q_2 = Q_1 + [(b) - (a)]$, the term $[(b) - (a)]$ is the difference between the heat evolved upon raising the products of reaction from T_1 to T_2 and that evolved in heating the reacting substances from T_1 to T_2. It is therefore the increase in heat capacity of the system during reaction, ΔC_p, multiplied by the temperature difference. If the heat capacity of a system increases during reaction, a larger quantity of heat will be absorbed in heating the reacting substances to this temperature, hence there will be a smaller heat evolution at the higher temperature. This is expressed by the equation

$$Q_2 = Q_1 - \Delta C_p(T_2 - T_1) \qquad (6)$$

when ΔC_p does not change with the temperature. If the heat capacities are functions of the temperature, as in the illustration just given, the equation is

$$\frac{dQ}{dT} = -\Delta C_p. \tag{7}$$

Before equation (7) can be integrated, each heat capacity must be expressed as a temperature function, $-\Delta C_p$ obtained by subtraction, and its proper value inserted in the equation. In the example above C_2 is $7.0 + 0.0071T - 0.00000186T^2$, C_1 is $9.75 + 0.0015T$, and $-\Delta C_p$ is therefore $2.75 - 0.0056T + 0.00000186T^2$. Substituting in equation (7) and integrating between the proper limits, we have

$$\int_{Q_1}^{Q_2} dQ = \int_{293}^{473} (2.75 - 0.0056T + 0.00000186T^2)\,dT$$

whence $(Q_2 - Q_1)$ is -150 cal., and Q_2 is $(Q_1 + 150)$ or 68,150 cal. as above.

This equation should not be applied in any case where there is a change in the *state of aggregation* of any substance involved upon heating from one temperature to another, for such a change takes place with the absorption or evolution of heat at a constant temperature, and cannot be included in the temperature function of specific heats. For example, if liquid water is formed at the lower temperature, and water vapor at the higher one, there is during heating of the reaction products a large absorption of heat with no attendant change of temperature when evaporation takes place. Let us consider the union of hydrogen and oxygen to form water vapor at 150°.

$$\begin{tikzcd}
\begin{array}{c} 2H_2 + O_2 \\ 150^\circ,\ 1\ \text{atm.} \end{array} \arrow[r, "Q_2"] & \begin{array}{c} 2H_2O\ (\text{gas}) \\ 150^\circ,\ 1\ \text{atm.} \end{array} \\
\begin{array}{c} 2H_2 + O_2 \\ 20^\circ,\ 1\ \text{atm.} \end{array} \arrow[u, "(a)"'] \arrow[r, "Q_1"] & \begin{array}{c} 2H_2O\,(\text{liquid}) \\ 20^\circ,\ 1\ \text{atm.} \end{array} \arrow[u, "(b)"']
\end{tikzcd}$$

Here Q_1 plus the change of state indicated by (*b*) must evolve the same quantity of heat as (*a*) plus Q_2, according to the law of conservation of energy. Now Q_1 is 68,400 cal. per mol of liquid water formed, or 136,800, and (*b*) is the sum of three steps, the value of each of which may be calculated: First heat two mols of liquid water from 20 to 100°, absorbing the quantity of heat $2 \times 18 \times 80 = 2{,}880$ cal.; second, evaporate this water at constant pressure, absorbing the heat $2 \times 18 \times 538 = 19{,}400$ cal.; third, heat the water vapor from 100 to 150°, absorbing 420 cal. per mol, as calculated on page 195. The sum of these quantities is 23,160; and the heat *evolution* corresponding to (*b*) is therefore −23,160 cal.

Also the heat absorbed by $2H_2 + O_2$ is 3 times the integral of $(6.5 + 0.001T)$ between the temperatures $T_1 = 293$ and $T_2 = 423$, since three mols of a diatomic gas are involved. The value of this integral is 4,625 cal. absorbed, or the heat *evolution* corresponding to (*a*) is −4,625 cal. Then

$$-4625 + Q_2 = -23{,}160 + 136{,}800; \text{ or } Q_2 = 118{,}265 \text{ cal.}$$

The heat *evolution* per mol of water vapor formed is thus 59,100 cal. at 150°. Final results of calculations should be rounded off in this manner, for writing 59,132.5 indicates a more exact result than is justified by either calculations or data.

A constant pressure has been assumed throughout these calculations of temperature effect. Similar considerations apply to constant volume changes. It is only necessary that the same total change of state be produced by each of two paths in order to equate the heat evolution of one path to that of the other path.

Calculation of Flame Temperatures.—The maximum temperature of a flame may be calculated by the principles explained in the previous paragraphs. In the oxy-acetylene flame, for example, water vapor and carbon dioxide are formed, and the thermochemical equation is

$$C_2H_2 + 2\tfrac{1}{2}O_2 = 2CO_2 + H_2O + 313{,}000 \text{ cal. at } 20°.$$

If no heat is lost to the surroundings, all of it is available for heating the products of reaction, and the highest temperature attainable with such a flame is the maximum which can be reached by adding 313,000 cal. to 88 grams of carbon dioxide and 18 grams of liquid water. This temperature follows from the specific heat equations:

$$313{,}000 = 1{,}440 + 9{,}700 + \int_{373}^{T}(7.0+0.0071T-0.00000186T^2)dT$$
$$+ 2\int_{293}^{T}(8.81 - 0.0019T + 0.00000222T^2)dT$$

where 1,440 cal. are required to heat a mol of liquid water to 100°, 9,700 cal. are required to vaporize it, and the other terms refer to heating a mol of water vapor and two mols of carbon dioxide. Integrated and simplified, this equation is

$$309{,}900 = 24.6T + 0.0017T^2 + 0.00000086T^3.$$

It is not necessary to apply the general solution of a cubic to this problem; a value of T is estimated and substituted into the right hand side of the equation; if it produces a smaller total than 309,900, the estimate was too low and a higher one should be made. In the present instance by estimating $T = 5{,}000$ the right hand side becomes 283,500, and by estimating $T = 5{,}300$ it is 324,500. Hence the maximum temperature reached is between these two absolute temperatures. As considerable heat is always lost to the surroundings, and combustion is not complete when just the theoretical quantity of oxygen is used, it is unlikely that the theoretical maximum will be reached, or approached within a few hundred degrees; and it is therefore unnecessary to estimate the available temperature more closely than this. For most calculations of this kind the molal heat capacity of carbon dioxide may be taken as $7.0 + 0.0028T$ and that of water vapor as $8.6 + 0.0030T$ without great error.

In making this calculation it has been assumed that water vapor and carbon dioxide were the only products formed, but if a temperature approaching 5000° is reached, considerable dissociation of the former into hydrogen and oxygen, and considerable dissociation of the latter into carbon monoxide and oxygen takes place. These dissociations will absorb heat, thus decreasing that available for raising the temperature of the products of combustion. Such calculations as that here given therefore represent the maximum attainable temperature under the most favorable conditions, and are always higher than the temperatures actually reached.

Questions

1. The heat of combustion of a gram of naphthalene at 20° is 9,612 cal. Calculate the heat of formation of a mol of it.

2. Calculate the heat required to raise 50 grams of bromine vapor from 63 to 150°C. *Ans.* 220 cal.

3. Calculate the heat evolved upon cooling a mol of steam at constant pressure from 200 to 100°. *Ans.* 840 cal.

4. How much heat will be required to raise a cubic foot of air (28 liters) from 0 to 100° at constant volume? At constant pressure?

5. The heat of solution of aluminum in HCl.200 *Aq* is 127,060 cal. per atomic weight, in HCl.20 *Aq* it is 126,000 cal. The heat of dilution of hydrochloric acid from HCl.20 *Aq* to HCl.200 *Aq* is 500 cal. per mol of acid. Calculate the heat of dilution of aluminum chloride solution.

6. The heat of solution of magnesium in HCl.200 *Aq* is 110,200 cal. per atomic weight. Calculate the heat of the reaction $3Mg + 2AlCl_3.Aq = 3MgCl_2.Aq + 2Al + x$ cal.

7. The heat of evaporation of water at 100° and constant pressure is 538.9 cal. per gram. Calculate the heat of evaporation at 150°. Over this small range of temperature the molal heat capacity of water vapor may be taken as $8.6 + 0.003T$.

8. When a gram of alcohol is burned at constant pressure 7,100 cal. are evolved. Calculate the heat evolution at constant volume.

9. Calculate the heat of formation of a mol of alcohol at constant pressure. Its heat of combustion is 7,100 cal. per gram.

10. The heat of evaporation of water at constant pressure (1 atmosphere) is 538.9 cal. per gram at 100°. Calculate the heat absorbed when a mol of water evaporates at 100° into an exhausted space, so that no work is done.

11. Anthracene (mol. wt. 178) melts at 216°, and absorbs 38.7 cal. per gram during fusion. Calculate the heat evolution if 10 grams of liquid anthracene are cooled to 150° and solidification is allowed to take place there. The specific heat of the liquid is 0.509, that of the solid is $0.28 + 0.0007t$, where t is the Centigrade temperature.

12. Calculate the heat evolution per gram of water which is undercooled to − 15° and there solidified. The latent heat of fusion is 79 cal. per gram at zero, and the specific heat of ice is half that of liquid water.

13. Compute the heat of combustion of octane by Thornton's rule and by Redgrove's rule, and the percentage error of each. The experimental value is 1,302,000 cal. per molecular weight (114.1 grams).

14. Estimate the heat of combustion of trimethylethylene by Redgrove's rule, and compare it with the result of experiment, 795,800 cal. per mol.

15. Carbon monoxide is manufactured by passing a mixture of oxygen and carbon dioxide over hot carbon. Since the oxidation of carbon evolves heat and the reduction of carbon dioxide by carbon absorbs heat, there is a mixture of oxygen and CO_2 which can be passed over carbon at 900°, where it will be changed to practically pure carbon monoxide without changing the temperature of the carbon bed. Calculate the heat of each reaction at

900°; and the composition of the gas mixture which will cause no change in temperature in the coke bed. At 20° the combustion of carbon evolves 97,000 cal. per mol of CO_2 formed, the combustion of a mol of CO evolves 68,000 cal., the atomic heat capacity of carbon may be taken as 4.0 cal. over the whole temperature range, the molal heat capacities of oxygen and CO are $6.5 + 0.001T$, and that of carbon dioxide may be taken as $7.0 + 0.0028T$.

16. At 25° $H_2 + I_2$ (solid) $= 2HI - 12{,}200$ cal.; between 25 and 400° the average specific heat capacity of hydrogen is 3.5 cal., that of HI is 0.055, and that of iodine vapor 0.034 cal. Assume the heat capacity of soild iodine to conform to the law of Dulong and Petit; the heat of sublimation of iodine at 75° is 56 cal. per gram. Calculate the heat of the reaction $H_2 + I_2$ (gas) $= 2HI + x$ at 400°.

17. Estimate the heat of formation of HBr from its elements at 500°. The boiling point of bromine is 59°, its latent heat of vaporization is about 40 cal. per gram. Estimate the heat capacity of liquid bromine from the law of Dulong and Petit (which, however, applies strictly only to solids) The following data are needed:

$$H_2 + Br_2\ (\text{liquid}) + Aq = 2HBr.Aq + 56{,}600\ \text{cal. at } 20°$$
$$HBr + Aq = HBr.Aq + 19{,}900\ \text{cal. at } 20°$$

For hydrogen C_p is $6.5 + 0.001T$ and for bromine vapor $C_p = 6.5 + 0.004\,T$. Assume 1 atmosphere throughout.

18. The heat evolved upon solution of one mol of hydrogen iodide in 100 Aq is 19,200 cal., the heat of solution of calcium oxide in water is 18,300 cal., and the heat of solution of calcium iodide is 27,700 cal. Calculate the the heat effect of adding a mol of calcium oxide (solid) to a large quantity of $HI.100Aq$. The other data needed are stated in the text.

19. The union of H_2 and O_2 in equivalent quantities to form water *vapor* at constant volume is attended by the evolution of 58,000 cal. per mol of water vapor formed at 20°. The heat of combustion of CO at 20° and constant volume evolves 68,000 cal. At what temperature is the heat of the reaction $CO + H_2O = CO_2 + H_2$ equal to zero? The molal heat capacity of CO_2 is $7.0 + 0.0028\,T$; for H_2, O_2, and CO it is $6.5 + 0.001T$.

CHAPTER VIII

EQUILIBRIUM IN HOMOGENEOUS SYSTEMS

One of the most important problems of physical chemistry has been the study of the conditions which govern the extent to which reactions take place. Most of the familiar reactions of inorganic chemistry, especially those of analytical chemistry, have been useful because they take place completely. In the gaseous reactions $H_2 + Cl_2 = 2HCl$ and $2H_2 + O_2 = 2H_2O$ as ordinarily carried out, there is after the reaction no appreciable quantity of the reacting substances remaining if they were put together in equivalent quantity. If an excess of hydrogen were added in the reactions, it would remain unchanged, and the yield of hydrogen chloride or of water would be just that corresponding to all of the chlorine or all of the oxygen.

In a considerable number of cases however, especially at higher temperatures, there is after the reaction has ceased a considerable quantity of *both* of the reacting substances left. Thus in the reaction $CO + H_2O = CO_2 + H_2$, if one mol of carbon monoxide and one of steam are placed together at 1,000°, the resulting mixture after all reaction has ceased (*i.e.*, at equilibrium) will be found to contain unchanged more than half of the water. If a mol of carbon dioxide and one of hydrogen are placed together, when equilibrium is reached the same relative quantities of the four substances will be found as when the reaction proceeded in the other direction; that is, somewhat more than half of the carbon dioxide and hydrogen will have reacted.

If we start with two mols of carbon monoxide and one of steam, a larger fraction of the steam will be reduced to hydrogen than when equal quantities were used, but the reaction does not proceed to the complete disappearance of any of the four substances, no matter what relative quantities are employed. Similarly the use of four mols of carbon dioxide with one of hydrogen will cause a much larger proportion of the hydrogen to form water. In general, an excess of any reacting substance increases the proportion of the substances formed from it, and decreases the proportion of the other substances reacting with the one in excess.

The laws of chemical equilibrium govern the relative quantities of substances present after equilibrium is attained, and are independent of the path by which this equilibrium was reached. Study of equilibrium will not, therefore, lead to definite conclusions as to the mechanism of a reaction. Thus if one mol of carbon monoxide, one mol of hydrogen, and a half mol of oxygen are mixed and exploded, the law of chemical equilibrium will describe the condition of the system when equilibrium is reached and practically all of the oxygen is used up. But it will give no indication of whether oxygen combined with carbon monoxide to form carbon dioxide, which then reacted with hydrogen; or whether oxygen reacted with hydrogen to form water, which was then attacked by the carbon monoxide. It is immaterial which path was followed, so far as the *final* state of the system is concerned.

Relation Among the Partial Pressures.—It has been found that the product of the partial pressures of carbon dioxide and hydrogen, divided by the product of the partial pressures of carbon monoxide and steam is always the same at equilibrium for a given temperature, no matter what relative quantities of the substances were present at the start. This may be expressed by the equation

$$\frac{p_{CO_2}p_{H_2}}{p_{CO}p_{H_2O}} = const.,$$

which is an expression of the *law of mass action*, or the law of chemical equilibrium. In words, this equation states that the product of the partial pressures of all the substance formed in a reaction, divided by the products of the partial pressures of all the substances reacting, is a constant for each reaction at a given temperature. The numerical value of the equilibrium constant changes considerably with temperature.

When more than one molecule of a substance is involved in the chemical equation of a reaction, the partial pressure of that substance in the equilibrium expression must be raised to the power which is its coefficient in the chemical equation. For example, the equation for the dissociation of hydrogen molecules into atoms at very high temperatures is $H_2 = 2H$, and the equilibrium expression is therefore

$$\frac{p_{\mathrm{H}}^2}{p_{\mathrm{H}_2}} = K.$$

Similarly in the reaction of the Deacon process for chlorine, $4HCl + O_2 = 2H_2O + 2Cl_2$, the equilibrium expression is

$$\frac{p_{\mathrm{H_2O}}^2 p_{\mathrm{Cl_2}}^2}{p_{\mathrm{HCl}}^4 p_{\mathrm{O_2}}} = K.$$

In reactions such as this one, it is important to know whether the water formed really exists as a vapor in the reacting mixture or whether, as a result of condensation liquid, water has been formed. In the latter case, the partial pressure of water would be only its vapor pressure at the temperature in question, regardless of the quantity which has been formed. The expression as written would contain this vapor pressure as the partial pressure of the water, and the equilibrium would be that corresponding to this pressure; not to the pressure calculated by assuming all of the water in the form of vapor.

In mass-action expressions in this book, partial pressures or concentrations of the *products* of a reaction as shown by a chemical equation will be written in the *numerator* of the equilibrium expression, and the pressures or concentrations of the reacting substances in the denominator. It will be evident that an incomplete reaction may be written in two ways, for example, $CO + H_2O = CO_2 + H_2$ or $CO_2 + H_2 = CO + H_2O$; and that according to which way it is written, the pressures of carbon monoxide and water may appear in either the numerator or denominator. The convention here adopted is the usual one now accepted by physical chemists, and it is a matter of indifference which way the chemical equation is written, so long as the equilibrium expression is written to correspond to it. Later we shall have occasion to consider the relation between equilibrium and the heat of the chemical reaction involved in it; the sign of which heat of reaction will also depend on which way the chemical reaction is written. All confusion will be avoided if the chemical reaction is always written down, the proper heat quantity affixed to the end of this equation (which is then also a thermochemical equation), and then the equilibrium expression is written to correspond with it. The choice of units in which to express the partial pressures is a matter of convenience, but in employing a given value of an equilibrium constant it is essential that the unit used in calculating it be adhered to in further calculations. Partial pressures are usually expressed in atmospheres or in millimeters of mercury; when concentrations are used, these are always mols per liter. As temperature has a considerable effect upon equilibrium, it is essential to state at what temperature the equilibrium constant was obtained, and in experimental work it is necessary to maintain this constant temperature while equilibrium is being reached.

Dissociation of Hydrogen.—Table 83 illustrates the effect of temperature upon the percentage dissociation of hydrogen molecules according to the chemical reaction $H_2 = 2H$. The equilibrium constant $p_{\mathrm{H}}^2/p_{\mathrm{H}_2} = K$, when the partial pressures are in millimeters of mercury, is shown, together with the fraction dissociated at each temperature when the total pressure is 1 atmosphere and when it is one millimeter. It will be noted that at lower pressures the fraction dissociated is much greater in each case. This is to be expected from the equilibrium expression. If the total pressure were suddenly reduced to one-tenth of its value (so quickly that no reaction took place), each partial pressure would be reduced to one-tenth of its original value. But since the pressure of the atoms is squared while that of the molecules is to the first power, the value of K has been reduced, and the system is no longer in equilibrium. It will therefore react to restore equilibrium by increasing the pressure of the atoms at the expense of the molecules, that is, dissociation will proceed until the ratio of $p_{\mathrm{H}}^2/p_{\mathrm{H}_2}$ returns to its proper value for the temperature in question.

This illustrates a general principle known as the law of Le-Chatelier-Braun, which states that a system to which a change of pressure is applied will react in such a way as to relieve that change of pressure. Thus if the pressure is decreased and the system expands, it will react in the direction which corresponds to an expansion. In the case above this was seen to take place. Similarly, if the pressure on the system is increased, a part of the increased pressure will be relieved by a decrease in the

TABLE 83.—DISSOCIATION OF HYDROGEN INTO ATOMS[1]

Absolute temperature	K (pressure in millimeters)	Fraction dissociated when	
		p = 760 mm.	p = 1 mm.
1,500	4.3×10^{-6}	0.000002	0.00005
2,000	0.0083	0.0033	0.087
2,500	0.78	0.0315	0.575
3,000	16.2	0.13	0.94
3,500	138.	0.34	0.993
4,000	710.	0.61	0.999

Change of equilibrium constant with the temperature is shown by the equation $\log K = 7.77 - 19{,}700/T$

number of gas particles (the single atoms act as molecules in their effect on the pressure), following the reaction $2H = H_2$.

General Law of Chemical Equilibrium.—This law, often called also the law of mass action, may be stated as follows: The product of the partial pressures of the substances formed in a reaction, each raised to a power which is the coefficient of its formula in the chemical equation, divided by the product of the partial pressures of the reacting substances, each raised to a power which is the coefficient of its formula in the chemical equation, is a constant when equilibrium is attained. Thus for the general reaction

$$aA + bB + \cdots = eE + fF + \cdots,$$

the condition of quilibrium at any specified temperature is

$$\frac{p_E^e p_F^f \cdots}{p_A^a p_B^b \cdots} = K_p. \tag{1}$$

The equation may be derived[2] from thermodynamics alone for a system of ideal gases, or for solutes which conform to the simple laws of ideal solutions. In this case the equilibrium expression is written in terms of the molal concentrations of the substances involved, *i.e.*,

$$\frac{C_E^e C_F^f \cdots}{C_A^a C_B^b \cdots} = K_c. \tag{2}$$

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[1] Langmuir, *J. Am. Chem. Soc.*, **37**, 417 (1915).

[2] Washburn, *J. Am. Chem. Soc.*, **32**, 472 (1910); G. N. Lewis, *Proc. Am. Acad. Sci.*, **43**, 259 (1907).

This law has been tested and confirmed experimentally, both for gaseous equilibrium and for equilibrium in solutions. Its deviations are usually not greater than those found between the measured and ideal properties of solutions or gases already considered. This law is perhaps the most important law of physical chemistry; its proper application will show what procedure is necessary to increase the yield of a desired product in a chemical reaction, or what should be done to decrease the yield of an undesirable product. It indicates the precautions to be observed in analytical chemistry, and enables us to calculate in solutions the extent to which a reaction will take place, the fraction of a substance hydrolyzed, the concentration of one substance from that of another, the quantity of a reagent necessary to convert one solid completely into another, and many other similar quantities which are of importance.

Study of Gaseous Equilibrium.—(*a*) It has already been stated that the conditions of equilibrium change with the temperature. This fact makes the study of equilibrium somewhat difficult, since a sample cannot be cooled for analysis without changing its composition in case the reaction is a rapid one. It is therefore necessary in most cases to measure the partial pressures or concentrations of substances by some physical method which does not remove any substance from the equilibrium mixture. One method of simplifying the study of equilibrium has been mentioned above. If any substance taking part in a gaseous reaction is also present as a liquid, its partial pressure in the system is at all times the vapor pressure of the pure substance. When this is determined in advance, one of the partial pressures is fixed by the presence of the liquid. From the chemical equation it is usually possible to establish relations among the partial pressures, such that from a single determination of the density of an equilibrium mixture it is possible to calculate all of the partial pressures.

The reaction between water vapor and sulfur, forming hydrogen sulfide and sulfur dioxide according to the equation

$$2H_2O + 3S = 2H_2S + SO_2$$

has been studied[1] in this simplified way, by employing an excess of sulfur in the reaction chamber. This chamber was immersed in a bath of boiling sulfur at 450° as shown in Fig. 36. The pressure of sulfur vapor at its boiling point is equal to that of the atmospheric pressure upon it; and since the sulfur in the reaction bulb was also at this temperature, the partial pressure of sulfur was obtained by reading the barometer at the time of the experiment. The equilibrium expression is therefore

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[1] Lewis and Randall, *J. Am. Chem. Soc.*, **40**, 362 (1918).

$$\frac{p^2_{H_2S}\, p_{SO_2}}{p^2_{H_2O}} = kp_S = K.$$

It is permissible to combine the value of k and the pressure of sulfur into a single constant K under these conditions, for in the presence of excess sulfur, its partial pressure in an equilibrium mixture is maintained constant at the vapor pressure of pure sulfur for the temperature in question. A weighed bulb of water and an excess of sulfur were introduced into the reaction vessel, and all of the air was pumped out. This was then sealed to a manometer tube, from which the total pressure could be determined, and suspended in a bath of boiling sulfur to maintain it at a constant temperature. The water was weighed in a very thin glass tube completely filled with liquid and sealed shut. When this was heated, expansion of the water burst the bulb and started the chemical reaction. Consider the water and sulfur at 450° before any reaction has taken place. The partial pressure of the water may be calculated from the simple gas law $pv = \frac{m}{18}RT$, from the weight of water employed and the

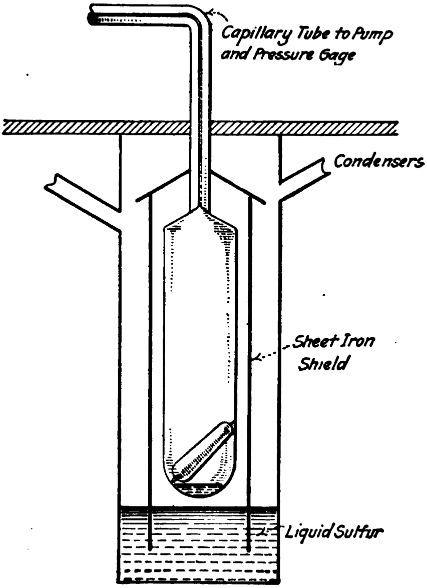

Fig. 36.

volume of the reaction chamber. The chemical reaction is $2H_2O + 3S = 2H_2S + SO_2$. Since a mol of hydrogen sulfide is formed for every mol of water reacting, the sum of the mols of water and hydrogen sulfide remains constant; hence, the sum of their partial pressures is at all times equal to the original pressure of the water vapor before the reaction occurred. The partial pressure of sulfur remains constant in the presence of liquid sulfur, for more sulfur vaporizes as the reaction proceeds. Any *increase* in pressure must therefore be due to the formation of sulfur dioxide.

Let us consider in detail the third experiment in Table 84, where the weight of water was 0.047 gram. The volume of the reaction chamber, after allowing for the space occupied by liquid sulfur, was 167 c.c.; the pressure of water vapor (in millimeters) before any reaction has taken place is calculated from the equation $\frac{p}{760} \times 167 = \frac{0.0470}{18} \times 82 \times (273 + 450)$, whence $p = 705$ mm. The barometric pressure was 766 mm., and this is therefore the sulfur pressure in the bulb. Then the total pressure before any reaction took place was $705 + 766 = 1{,}471$; and the measured equilibrium pressure was 1,519 mm. As shown by the chemical equation, if the pressure of sulfur is kept constant, any *increase* in pressure must be due to the formation of sulfur dioxide, since the sum of the partial pressures of water and hydrogen sulfide remains unchanged. Then $1{,}519 - 1{,}471 = 48$ is p_{SO_2}. The chemical equation further shows that there are two molecules of hydrogen sulfide formed for every molecule of sulfur dioxide, hence the partial pressure of hydrogen sulfide must be $2p_{SO_2}$ or 96 mm. But $96 + p_{H_2O} = 705$, or $p_{H_2O} = 609$. The equilibrium constant is therefore $(96)^2(48)/(609)^2 = 1.19$. It is usual in equilibria of this kind to include the partial pressure of the substance present as a liquid or solid in the value of the equilibrium constant. Thus the constant 1.19 is really $k \times p_s$, but since each of these is constant, the calculation is simplified to this extent. For cases in which the sulfur pressure is not kept constant by the presence of an excess of its liquid, this equilibrium constant does not, of course, apply.

TABLE 84.—EQUILIBRIUM IN THE REACTION BETWEEN SULFUR AND WATER. THE PARTIAL PRESSURES ARE SHOWN IN MILLIMETERS OF MERCURY AND ARE SO EMPLOYED IN COMPUTING THE EQUILIBRIUM CONSTANT

Grams water	Volume cubic centimeters	Pressure calculated for no reaction	Observed equilibrium pressure	p_{SO_2}	p_{H_2S}	p_{H_2O}	p_S	$K_p = \frac{p^2_{H_2S}\, p_{SO_2}}{p^2_{H_2O}}$
0.0441	151	1,501	1,554	53	106	624	771	1.52
0.0549	204	1,435	1,476	41	82	592	761	0.80
0.0470	167	1,471	1,519	48	96	609	766	1.19
0.0540	117	1,913	1,978	65	130	1,019	764	1.06
						Average	....	1.17

Concordance among the constants obtained is not all that could be desired, but the difficulties in making measurements are very great. An error of one-half of 1 per cent in the total pressure is 7 mm. but since the small partial pressure of sulfur dioxide is obtained by subtracting the calculated total pressure from the observed total pressure, this 7 mm. error will appear as 7 mm. on the total of only 46 mm. pressure of sulfur dioxide, or an error of 15 per cent. The experimental error is thus increased thirty fold. Considering this, it is remarkable that the constants agree so well.

Similar considerations apply in case one of the reacting substances is also present as a solid phase, for at every temperature the sublimation pressure of a solid is a characteristic property of it, unchanged by the presence of other gases. A determination of this sublimation pressure in a separate experiment establishes its partial pressure in the equilibrium mixture for the temperature in question.

(*b*) In reactions involving hydrogen at quite high temperatures, advantage is taken of the fact that platinum is permeable to this gas and not to other gases. Thus a platinum tube inserted into a reaction chamber allows free penetration of hydrogen, and its partial pressure is measured by a manometer attached to the platinum tube. This method has been applied to the equilibrium

$$CO_2 + H_2 = CO + H_2O$$

at high temperatures.[1] A gaseous mixture containing known proportions of carbon dioxide and hydrogen was brought to equilibrium at a total pressure of 1 atmosphere. As the total number of mols of gas does not change during the chemical reaction, no change of pressure is observed. But a decrease in hydrogen pressure can take place only when water is formed from it; hence the difference between the starting pressure of hydrogen (calculated from its mol fraction in the original mixture) and the equilibrium pressure represents water-vapor pressure. From the chemical reaction it follows that there is a mol of carbon monoxide formed for each mol of hydrogen used, *i.e.*, for each mol of water formed. And there is a mol of carbon dioxide used up for every mol of carbon monoxide formed. Thus a measurement of hydrogen pressure gives (*a*) the partial pressure of hydrogen, (*b*) the partial pressure of carbon monoxide, (*c*) the partial pressure of water vapor, (each of these last two being equal to the decrease in hydrogen pressure during reaction) and by difference (*d*) the pressure of carbon dioxide. Table 85 shows the results of experiments at 986°, together with values of the constant

$$\frac{p_{\mathrm{CO}}p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}p_{\mathrm{CO_2}}} = K_p.$$

TABLE 85.—EQUILIBRIUM AT 986°

Original mixture		Equilibrium mixture			
Per cent CO_2	Per cent H_2	Per cent CO_2	Per cent $CO = H_2O$	Per cent H_2	K_p
10.1	89.9	6.69	9.4	80.5	1.60
30.1	69.9	7.15	22.96	46.93	1.58
49.1	51.9	21.22	27.90	22.95	1.60
60.9	39.1	34.43	26.45	12.67	1.60
70.3	29.7	47.50	22.82	6.85	1.60
			Average	....	1.596

An interesting feature of this equilibrium is the calculation of dissociation constants from it. So far nothing has been said about the presence of oxygen in this mixture, and there is in fact only an insignificant quantity present. Its partial pressure would have no effect upon the total pressure which could be detected by experimental means. But the small quantity of it present must satisfy the dissociation equilibria $2H_2O = 2H_2 + O_2$ and $2CO_2 = 2CO + O_2$, for which the equations are

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[1] Hahn, *Z. physikalische Chem.*, **44**, 513 (1903).

$$\frac{p^2_{H_2} p_{O_2}}{p^2_{H_2O}} = K_{H_2O} \quad \text{and} \quad \frac{p^2_{CO} p_{O_2}}{p^2_{CO_2}} = K_{CO_2}.$$

Upon dividing the second of these dissociation expressions by the first, and extracting the square root, we obtain

$$\frac{p_{CO} \, p_{H_2O}}{p_{H_2} \, p_{CO_2}} = \sqrt{\frac{K_{CO_2}}{K_{H_2O}}} = K,$$

which is the equilibrium expression given above for the reaction $CO_2 + H_2 = CO + H_2O$. This furnishes a means of calculating equilibrium constants from dissociation constants, or of calculating dissociation constants from measurements of equilibria such as this one.

(*c*) Other methods are applicable to certain types of equilibrium; thus a determination of the density of an equilibrium mixture establishes the mol fraction of each constituent in the dissociation of phosphorus pentachloride. Let x be the fractional dissociation into phosphorus trichloride and chlorine, and let D be the weight of a liter of equilibrium mixture at the temperature T. Then for each formula weight of pentachloride put into the mixture, x mols of chlorine and x mols of trichloride form, and $(1 - x)$ mols of pentachloride remain. The mol fraction of chlorine is therefore $x/(1 + x)$, since $1 + x$ is the total number of mols present per formula weight of pentachloride; this is also the mol fraction of trichloride, and $(1 - x)/(1 + x)$ is the mol fraction of pentachloride. At a temperature T the volume of a mol of mixture is RT/p liters, where p is the total pressure in atmospheres, and R is 0.082. If D is the weight of a liter, a mol of mixture weighs DRT/p grams. The molecular weights of chlorine, trichloride and pentachloride being respectively, 71, 137.4 and 208.3, and the number of mols of each in a mol of mixture being the mol fraction of each, we have

$$\frac{x}{1 + x} 71 + \frac{x}{1 + x} 137.4 + \frac{1 - x}{1 + x} 208.3 = \frac{DRT}{p},$$

from which the fractional dissociation may be calculated.

(*d*) In other cases one of the reacting substances may have a characteristic color which varies with its concentration; this may then be determined by comparison with color standards containing that substance alone in known quantity. Other methods must often be devised to fit the problem in hand, but these may serve as illustrations of typical methods for studying gaseous equilibrium.

Equilibrium in solution may be studied by the conductivity of a solution as a whole (which measures the ion concentrations, but not those of non-ionized substances), from determinations of the vapor pressure of some constituent which is volatile, from distribution of a solute between the phase under examination and a second phase in which only one reacting substance is soluble, from freezing point depressions in case the equilibrium does not change much with the temperature, or from the color of a solution produced by one of the substances. As in the case of gaseous equilibrium, the concentration of one substance may often be expressed in terms of the concentration of some other constituent.

Equilibrium in Solution. Ionization.—When the law of mass action is applied to the equilibrium between a dissolved substance and its ions, the chemical equation is, taking acetic acid as an example, $HAc = H^+ + Ac^-$, and the equilibrium expression is

$$\frac{(H^+)(Ac^-)}{(HAc)} = K. \tag{3a}$$

We shall enclose the symbol of a substance in parenthesis to indicate the concentration of it; thus in the previous equation (H^+) is used to denote the concentration of hydrogen ion in the solution, rather than C_{H^+}. This equation may be tested by means of conductivity data, since the fraction ionized is shown by the conductivity ratio $\gamma = \frac{\Lambda}{\Lambda_0}$, the concentration of each of the ions in a solution of concentration C is $C\gamma$, and the concentration of the non-ionized molecules is $C(1 - \gamma)$. The mass-action expression thus reduces to

$$\frac{(C\gamma)^2}{(1-\gamma)C} = K. \tag{3}$$

Table 86 shows the value of this constant for acetic acid.

TABLE 86.—IONIZATION CONSTANT OF ACETIC ACID AT 18°

Concentration	$(C\gamma)^2/C(1-\gamma) = K$
0.001	1.77×10^{-6}
0.004	1.80
0.01	1.79
0.02	1.79
0.10	1.80
1.0	1.8

Satisfactory ionization constants are obtained for such substances as ammonium hydroxide, acetic and other organic acids, carbonic acid, phosphoric acid and nitrous acid. A table of these constants, for use in solving problems, is given below. It should be noted that the ionization constant of any acid HA which conforms to the law of chemical equilibrium is

$$\frac{(\mathrm{H}^+)(\mathrm{A}^-)}{(\mathrm{HA})} = K \tag{3b}$$

and that the expression (H^+) indicates the total concentration of hydrogen ions, not just that part of it due to the particular acid in question. Thus in the presence of a mineral acid which is quite highly ionized, the hydrogen ion concentration would be far higher than from a weak acid alone. Equation (3*b*) describes the ionization of the weak acid under these conditions, and the total hydrogen ion concentration is taken into account.

When more than one acid is present, equation (3) should not be used, but an equation like (3*b*) applies. For example, if 0.10 formal acetic acid is mixed with an equal volume of 0.10 formal hydrochloric acid, so that each acid concentration is 0.05, the weaker acetic acid will have no appreciable effect upon hydrochloric acid, which is ionized about 90 per cent. The hydrogen ion concentration is therefore about 0.045, and only a very small part of it comes from acetic acid; the acetate ion concentration is 0.05γ, and the concentration of non-ionized acetic acid is $0.05\ (1 - \gamma)$. Upon substituting these values into equation (3*b*), putting 18×10^{-6} for K, and solving for γ, we find that the acetic acid is only 0.04 per cent ionized in the presence of an equal quantity of hydrochloric acid; while it is 3 per cent ionized at 0.05 formal in the absence of this acid.

Similar considerations would apply to any weak acid in the presence of a strong acid; to any weak base in the presence of a strong base; and to a weak acid or a weak base in the presence of its salts. For example, if 0.1 formal ammonium hydroxide is mixed with an equal volume of 0.1 formal ammonium chloride solution, the base in the resulting solution is only 0.04 of 1 per cent ionized. This explains why the relatively insoluble hydroxides of magnesium and ferrous iron are not precipitated by ammonium hydroxide in the presence of ammonium salts. Such exceedingly insoluble hydroxides as ferric hydroxide or aluminum hydroxide are precipitated even in the presence of ammonium salts; for the hydroxide ion concentration required is very small, and is reached even in the presence of large concentrations of ammonium ions.

TABLE 87.—IONIZATION CONSTANTS AT 25°

Formic acid........	214×10^{-3}	Carbonic acid.....K_1	3.5×10^{-7}
Acetic acid.........	18×10^{-6}	K_2	4×10^{-11}
Propionic acid......	14.5×10^{-6}	Ammonia...........	18×10^{-6}
Acetoacetic acid....	150×10^{-6}	Pyridine............	23×10^{-10}
Chloroacetic acid ..	$1{,}550 \times 10^{-6}$	Aniline..............	4×10^{-10}
Benzoic acid........	60×10^{-6}	Hydrocyanic acid....	7×10^{-10}
Nitrous acid........	450×10^{-6}	Boric acid...........	6.6×10^{-10}
Hydrofluoric acid...	$7{,}000 \times 10^{-6}$	Phenol..............	1.1×10^{-10}
Phosphoric acid..K_1	10^{-2}		
K_2	2×10^{-7}		
K_3	3.6×10^{-13}		

Partly from Kendall, *J. Am. Chem. Soc.*, **39**, 2,317 (1917); Lunden, *J. chimie physique*, **5**, 574 (1907); Boyd, *J. Chem. Soc. London*, **107**, 1,538 (1915).

Highly Ionized Substances.—When the "ionization constants" are calculated for salts, highly ionized acids, and bases in a similar way, there is found no constant value. In other words, *the law of mass action does not apply to the ionization of a salt.* Up to the present, no satisfactory explanation for this anomaly has been found. The mass-action law applies to cases not involving ionized substances so well that it is natural to inquire if the theory of ionization is at fault But the ionization theory has been so useful in explaining abnormally large freezing point depressions, in showing why all acids are sour, why all chlorides precipitate silver chloride when silver nitrate is added, why all copper salts are blue when dissolved in water, and in explaining the mechanism of electrolytic conduction, that one is not ready to discard it. At present there exists only a sort of compromise, accepted for lack of a better explanation, but recognized as highly unsatisfactory.

The law of mass action may not be expected to hold rigorously except for ideal solutes, but the deviations to be expected from it are not more than those between other observed and calculated properties of solutions. One is quite unprepared for such wide discrepancies as those shown[1] by the ionization "constants" of Table 88. The equilibrium "constant" is not even roughly constant, but increases a hundred fold for potassium chloride and a million fold for potassium ferrocyanide.

TABLE 88.—"IONIZATION CONSTANTS" FOR SALTS OF DIFFERENT TYPES

KCl		$Ba(NO_3)_2$		$K_4Fe(CN)_6$	
Concentration	*K*	Concentration	*K*	Concentration	*K*
0.0001	0.0075	0.001	0.000017	0.0005	0.7
0.001	0.035	0.005	0.00018	0.0020	18.0
0.01	0.132	0.01	0.00045	0.012	1,171.
0.1	0.495	0.10	0.97	0.1	41,190.
1.0	2.22	.....	....	0.4	842,100.

Since the law of chemical equilibrium may be derived from thermodynamics for ideal solutes, it is clear that some or all of the molecular species involved in the equilibrium between a salt and its ions are very far from ideal solutes. The law of mass action holds in solutions where no ions are involved; it would be natural in view of this to state that the ions are not "normal" solutes and ascribe all of the abnormal behavior to them on account of their electric charges. But as far as can be judged from their behavior, ions appear to obey the laws of ideal solutes, to a fairly close approximation at least, and we are thus forced to place the responsibility for these anomalies chiefly upon the non-ionized portion of the electrolyte.

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[1] Lewis, *Z. physik. Chem.*, **70**, 215 (1909). Printed in English.

It has been suggested that there is no satisfactory method of measuring the extent of ionization, and that this is the real difficulty. If, as mentioned at the end of the chapter on electrical conductivity, ionization is practically complete, there is of course no non-ionized substance present, and its concentration cannot be included in a mass-action expression. But by assuming complete ionization of salts the difficulties are not removed; rather they are made greater in many instances. Certainly nothing is to be gained in the treatment of moderately ionized electrolytes by this bold assumption, and much would be lost so far as slightly ionized bases and acids are concerned. If salts and "strong" acids are completely ionized, while "weak" electrolytes are not completely ionized, the difficulty of drawing a line between these two classes of electrolytes appears at once. And while it is quite true that the "activity," or mass-action effect of an ion is not equal to that calculated by multiplying the salt concentration by $\frac{\Lambda}{\Lambda_0} = \gamma$ when the conductivity ratio is taken as a measure of ionization; it is equally true that the activity of an ion is not equal to the total salt concentration. In solutions less than 1 normal the "activity" is *less* than the ion concentration $C\gamma$, so that an assumption of complete ionization leads to an increased error in calculated mass-action effects.

Empirical Ionization Equations.—Many attempts have been made to find some law which governs the change of the ionization with concentration for salts and other highly ionized substances, most of which are based on some empirical alteration in the mass-action expression $(C\gamma)^2/(1 - \gamma)C = K$. The equation of Storch is

$$\frac{(C\gamma)^n}{(1 - \gamma)C} = K \tag{4}$$

and it has been found by trial that the value of n is between 1.40 and 1.55 for all types of salts, and over a wide range of temperature.[1] If the value of n is taken as 3/2 the equation becomes the Rudolphi formula. While this equation expresses the change of ionization quite well for moderate concentrations, it does not reduce to the law of mass action for very low salt concentrations where this law is valid for electrolytes.[1]

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[1] Noyes, *Science*, **20**, 584 (1904); *J. Am. Chem. Soc.*, **30**, 335 (1908); Sherrill, *J. Am. Chem. Soc.*, **32**, 741 (1910).

To adapt this equation and the law of mass action to their respective concentration ranges, Kraus and Bray[2] combined the equation of Storch with the mass-action law into the form

$$\frac{(C\gamma)^2}{C(1 - \gamma)} = K + D(C\gamma)^m \tag{5}$$

in which K is the mass action constant, D and m are constants for each substance studied, and C and γ have their usual significance. When the concentration is small the term containing D becomes small in comparison to K, and the equation assumes the form of the familiar mass-action law. When the concentration is large, K is small compared to the D term, and the equation becomes that of Storch. A test of this equation for all of the available data in solvents other than water as well as in aqueous solutions shows that it describes the change of conductance with concentration if the ratio $\frac{\Lambda}{\Lambda_0} = \gamma$ is taken as a measure of the fractional ionization. The disadvantage of the equation is that the constants K, D, and m, must be determined for each substance in each solvent by at least three measurements of conductivity at different concentrations. The simpler equations to which it reduces at high and at low concentrations will on that account be found much more useful. In considering a salt for which the value of n in the Storch equation is not known, satisfactory calculations can be made by taking $n = 1.5$.

Ionization in Salt Mixtures.—When two salts with an ion in common, such as two chlorides or two potassium salts, are present in solution, each exerts an influence on the ionization of the other. This effect is not to be calculated from the simple law of mass-action, just as the ionization of a single salt is not so calculated. But the effect of each salt upon the other can be calculated from the Storch equation, or from the Kraus equation, provided the values of the characteristic constants for each salt are known.

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[1] Washburn, *J. Am. Chem. Soc.*, **40**, 145 (1918).

[2] *J. Am. Chem. Soc.*, **35**, 1,315–1,434 (1913).

Such calculations are quite complicated, but the results of them lead to calculated equivalent conductivities for mixtures which accord closely with the results of experiment.[1]

In place of performing these calculations when salt mixtures are involved, we shall make an assumption which is nearly in accord with the results of them, namely that each salt in the mixture is ionized to the same extent as when it is present alone at the total salt concentration. For example, in a mixture in which sodium nitrate is 0.5 formal and potassium nitrate is 0.05 formal, we shall assume that the fractional ionization of the sodium salt is the same as that in a solution 0.55 formal in sodium nitrate; and we shall assume that the ionization of the potassium salt is the same as in a solution 0.55 formal in potassium nitrate. Since nearly all salts of the same type ionize to about the same extent in solutions of equal concentration, this is equivalent to assuming that in a salt mixture, each substance has the same fractional ionization as the other, regardless of their relative concentrations in the mixture.

Polybasic Acids.—Weak acids, such as phosphoric acid, carbonic acid, tartaric acid and hydrogen sulfide, ionize in steps, and a mass-action expression may be written for each step. For example, carbonic acid gives in its first-step ionization hydrogen ions and bicarbonate ions, H^+ and HCO_3^-, and the corresponding mass-action expression is

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 3.5 \times 10^{-7} = K_1.$$

The bicarbonate ion itself acts as a weaker acid than carbonic acid from which it came, and ionizes into hydrogen ions and carbonate ions, $HCO_3^- = H^+ + CO_3^{--}$.

$$\frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = 4 \times 10^{-11} = K_2.$$

It should be noted that K_2 is written for the *ionization of an ion* into other ions. The expression (H^+) in the numerator of K_2 indicates total hydrogen-ion concentration in solution, not merely that part of it which came from the ionization of bicarbonate ions. From the very small ionization constant K_2 it is seen that only an exceedingly small concentration of carbonate ions ever exists in the presence of a moderate hydrogen-ion concentration. This explains the ready solubility of carbonates in acid, since their carbonate ions are immediately converted into bicarbonate ions as soon as they pass into solution. From these constants the ratio of the carbonate ion concentration to the bicarbonate ion concentration, for example, can be calculated when the hydrogen ion concentration is known.

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[1] Bray and Hunt, *J. Am. Chem. Soc.*, **33**, 781 (1911); Sherrill, *J. Am. Chem. Soc.*, **32**, 741 (1910); Mackay, *Ibidem*, **33**, 308 (1911). These papers give a more exact, but more complicated, statement of ionization in salt mixtures.

The first-step ionization of phosphoric acid does not conform very closely to the law of mass action, but the second and third steps correspond to the ionization of very weak acids,[1] and do conform to this law. The chemical equations are $H_2PO_4^- = H^+ + HPO_4^{--}$ and $HPO_4^{--} = H^+ + PO_4^{---}$; the mass-action equations are

$$\frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)} = 2 \times 10^{-7} = K_2;$$

and

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = 3.6 \times 10^{-13} = K_3.$$

Let us consider in detail the titration of sodium carbonate with an acid, by means of an indicator which shows when practically all of the carbonate has been changed to bicarbonate, and compute the error of such a titration. If the error of this titration is to be less than 1 per cent, the titration must not cease until the ratio of unchanged carbonate to bicarbonate ions is less than 1 : 100. Upon substituting in the equation for K_2 of carbonic acid the ratio $(CO_3^{--})/(HCO_3^-) = 1/100$, the hydrogen ion concentration is calculated as 4×10^{-9}. A proper indicator will not, therefore, change its color before this point is reached. Now substitute in the equation for K_1 the value of hydrogen ion concentration just calculated, and solve for the ratio of bicarbonate to free carbonic acid. This ratio must be large if the titration is to be accurate, for free carbonic acid can come only from bicarbonate ions reacting with more standard acid. When the hydrogen ion concentration is 4×10^{-9}, the ratio of bicarbonate ion concentration to free carbonic acid is 90 : 1, which shows that the second stage of titration, by which bicarbonate is converted to free carbonic acid, has progressed about 1.1 per cent when the first stage is 1.0 per cent short of completion. As these two errors affect the volume of acid used in opposite directions, the *net* error of titration is 0.1 per cent, if the indicator changes color at the proper hydrogen ion concentration. Any other concentration of hydrogen ion at the end point will increase one of these errors while decreasing the other, but will not bring the total error appreciably under 0.1 per cent. A method of choosing the indicator will be given presently.

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[1] Abbott and Bray, *J. Am. Chem. Soc.*, **31**, 729 (1909).

Equilibria Involving Ions.—There are many chemical reactions which appear to take place between ions, and whose equilibrium conditions depend only upon the ion concentrations involved. It is customary, in formulating equilibrium expressions for these reactions, to leave out of consideration the concentrations of non-ionized molecules of strong electrolytes, and to consider the ions as solutes which conform to the mass-action law. While this procedure is not a very satisfactory one, it leads to approximate agreement with the experimentally determined values, and is much more satisfactory than any empirical expression which attempts to include the concentrations of salt molecules together with the ion concentrations. In these expressions the molecules of weak electrolytes are considered, since they conform to the mass-action law. For example, the reaction between a salt of a weak acid like acetic acid and another acid such as nitrous acid would be

$$\mathrm{NaAc} + \mathrm{HNO_2} = \mathrm{NaNO_2} + \mathrm{HAc},$$

the equilibrium expression for which is written

$$\frac{(\mathrm{HAc})(\mathrm{Na^+})(\mathrm{NO_2^-})}{(\mathrm{Na^+})(\mathrm{Ac^-})(\mathrm{HNO_2})} = K;$$

and the equilibrium expression for the hydrolysis of ammonium acetate, $\mathrm{NH_4Ac} + \mathrm{H_2O} = \mathrm{NH_4OH} + \mathrm{HAc}$, is written

$$\frac{(\mathrm{NH_4OH})(\mathrm{HAc})}{(\mathrm{NH_4^+})(\mathrm{Ac^-})} = K.$$

When the equilibria are so formulated, a value of K is obtained from experiments which enables us to calculate correctly the concentrations at equilibrium in another system involving the same substances. The concentration of water in a solution which is dilute does not change as the reaction progresses, and this concentration is understood to be included in the value of K for the hydrolysis. In the presence of ammonium acetate, the fractional ionization of acetic acid is negligibly small, for the high concentration of acetate ions necessitates a very small concentration of hydrogen ions. Ammonium hydroxide in the presence of an ammonium salt is not appreciably ionized. Similarly, in the reaction above, nitrous acid does not ionize to an appreciable extent in the presence of sodium nitrite and acetic acid does not ionize in the presence of sodium acetate. These acids can therefore be treated as if all of each one present were in the non-ionized state.

In formulating mass-action expressions in the way just explained, we are not assuming complete ionization of salts. For example, in the reaction between sodium acetate and nitrous acid formulated above, the nitrite ion concentration is $C\gamma$, where γ is the fractional ionization. There is no reason for ignoring the non-ionized portion of sodium nitrite except that better mass-action constants are obtained when this is done. This is of course highly unsatisfactory as a general procedure, but it is about the best that can be done at present. Further research is needed to explain the behavior of ions, and until this is at hand, we shall adopt the simple procedure of ignoring the non-ionized portion of salts. We shall at the same time assume that all salts involved in an equilibrium mixture have the same fractional ionization. This is not true within 2 or 3 per cent, but no better accuracy than this is to be expected in equilibria involving the ions of salts in any case.

The Ionization of Water.—Measurements of the conductivity of pure water, made primarily to determine the correction to be applied in calculating the conductivity of dilute solutions, have led to the conclusion that the concentration of hydrogen ion in it is 10^{-7} formal, or one equivalent of hydrogen ion in ten million liters of water; the concentration of hydroxide ion, OH^-, in pure water is also 10^{-7}. These ions result from the ionization of water itself, $H_2O = H^+ + OH^-$, not from the presence of impurities in it. Considerations such as we are about to take up have shown that the product of these ion concentrations is a constant in all water solutions for a given temperature. Thus the product $(H^+)(OH^-) = 10^{-14} = K_w$ is constant for a temperature, of 25°, whatever the other substances present. This means that in a solution of a base where the concentration of hydroxide ions is quite high, the hydrogen-ion concentration is correspondingly reduced, and in a solution of an acid the hydroxide ion concentration is correspondingly reduced. As is the case with most equilibria, this ion product changes with the temperature. It will be noticed that in spite of the fact that water is an extremely weak electrolyte (*i.e.*, a very slightly ionized one) we have not included the non-ionized portion of it in the equilibrium expression. This might have been written $(H^+)(OH^-) = K'(H_2O) = K_w$, where the term K_w is understood to include the concentration of the water molecules. There is a difficulty in considering the concentration of a solvent when it is thought of as a dissolved substance at the same time; but to avoid this, it is only necessary to notice that the water present in a dilute solution is practically constant at all times, and that therefore its mass-action effect is constant. The product of this mass-action effect and the constant K' above is K_w, called the ionization constant of water. Its value for several temperatures is shown below.

TABLE 89.—IONIZATION CONSTANT OF WATER AT VARIOUS TEMPERATURES

Temperature	Values of $K_w \times 10^{14}$ as determined by				
	Noyes[1] Kanolt[6]	Lunden[2]	Lorenz and Bohi[3]	Heydweiller[4]	Kohlrausch[5]
0°	0.089	....	0.136	0.116	
18°	0.46	0.31 (10°)	0.716	0.59	0.78
25°	0.82	1.05	1.216	1.04	1.05
50°	4.5	5.17	8.75	5.66	
75°	16.9	....	28		
100°	48	....	73	58.2	

[1] *Carnegie Inst. Publ.*, **63**, 346 (1907); *J. Am. Chem. Soc.*, **32**, 159 (1910).

[2] *J. chimie physique*, **5**, 574 (1907). Hydrolysis of ammonium borate.

[3] *Z. physik. Chem.*, **66**, 733 (1909). E.m.f. of acid-alkali cell.

[4] *Annalen der Physik* (4), **28**, 503 (1909). Heat of neutralization.

[5] *Wied. Annalen*, **53**, 209 (1894). Conductivity of pure water.

[6] *J. Am. Chem. Soc.*, **29**, 1,402 (1907). Hydrolysis of ammonium salts.

Hydrolysis.—When a salt like potassium cyanide is dissolved in water, the cyanide ions from it find themselves in the presence of a small concentration of hydrogen ions from the ionization of water. Hydrocyanic acid is only very slightly ionized and the concentration of cyanide ions is quite high; there is a marked tendency of the ions of the acid to combine into electrically neutral molecules, and this takes place. This leaves potassium ions and hydroxide ions together, but these have little tendency to combine since potassium hydroxide ionizes readily. To make up the loss in hydrogen ions in the formation of hydrogen cyanide, more water molecules ionize, and the chemical reaction

$$\mathrm{KCN} + \mathrm{H_2O} = \mathrm{KOH} + \mathrm{HCN}$$

proceeds until equilibrium is established. This reaction is called hydrolysis; it will be seen that it is the reverse of neutralization. Potassium cyanide is about 1.2 per cent hydrolyzed in 0.1 formal solution at 25°, about 3.5 per cent hydrolyzed at 0.01 formal, and about 12 per cent hydrolyzed at 0.001 formal. Following the convention adopted above (of writing equilibrium expressions in terms of the ions of largely ionized substances), and leaving out of the formulation the concentration of the water, since it is essentially unchanged by the small quantity of it reacting, we have

$$\frac{(\mathrm{K^+})(\mathrm{OH^-})(\mathrm{HCN})}{(\mathrm{K^+})(\mathrm{CN^-})} = K_h$$

as the equilibrium expression for the reaction. The concentration of potassium ion may be cancelled from the expression, and if we multiply both numerator and denominator by the concentration of hydrogen ion, we have

$$\frac{(\mathrm{H^+})(\mathrm{OH^-})(\mathrm{HCN})}{(\mathrm{H^+})(\mathrm{CN^-})} = K_h.$$

It will be seen that this expression is the quotient of the expression $(\mathrm{H^+})(\mathrm{OH^-}) = K_w$ divided by the ionization expression for hydrocyanic acid, $(\mathrm{H^+})(\mathrm{CN^-})/(\mathrm{HCN}) = K_a$, and since each of these values is known, we have at once a method of evaluating the equilibrium constant without recourse to separate measurements of this particular equilibrium. Cancelling out now the hydrogen ion concentration (which was inserted merely to make clear the method of evaluating the constant), we have

$$\frac{(\mathrm{OH}^-)(\mathrm{HCN})}{(\mathrm{CN}^-)} = K_h = \frac{K_w}{K_a}. \tag{6a}$$

Now denoting by C the formal concentration of potassium cyanide, by γ the fraction of each salt ionized,[1] and by h the fraction of the salt which has undergone hydrolysis, the concentration of hydrocyanic acid is hC, the concentration of potassium hydroxide is also hC and that of the hydroxide ion is therefore $hC\gamma$, the concentration of the remaining potassium cyanide is $(1 - h)C$ and that of the cyanide ion is therefore $(1 - h)C\gamma$. Substituting in the above expression for equilibrium, we have as the general equation for this type of hydrolysis

$$\frac{hC\gamma \cdot hC}{(1 - h)C\gamma} = \frac{K_w}{K_a} = K_h. \tag{6}$$

When the salt of a strong acid and a weak base hydrolyses, the expression for its fraction hydrolyzed may be derived in a manner exactly similar to that for the case of potassium cyanide just considered, and, putting K_b for the ionization constant of the weak base, the resulting equation may be written

$$\frac{hC\gamma \cdot hC}{(1 - h)C\gamma} = \frac{K_w}{K_b} = K_h. \tag{7}$$

There remains to be considered the case where both the acid and base of a salt are slightly ionized. Here there is a tendency for the positive ions of the salt to combine with the hydroxide ions of water, added to a tendency of the negative ions of the salt to combine with hydrogen ions from water. When both ions are thus removed, the hydrolysis will proceed much farther.

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[1] When two simple di-ionic salts having an ion in common (the potassium ion in this case) are present in a solution, the fraction of each one ionized is about equal to that for each salt if it were alone present at the total salt concentration. Thus the ionization of potassium hydroxide in this solution is about that of a solution C formal in potassium hydroxide, and the ionization of potassium cyanide in the mixture is about equal to that of a solution C formal in potassium cyanide. These fractional ionizations are approximately equal, and may be assumed identical in such calculations as this.

We may write the chemical equation, taking ammonium acetate as an example,

$$NH_4Ac + H_2O = NH_4OH + HAc$$

and the equilibrium expression is

$$\frac{(NH_4OH)(HAc)}{(NH_4^+)(Ac^-)} = K_h. \tag{8a}$$

It is permissible here, as in the case before, to neglect the ionization of ammonium hydroxide and of acetic acid in the presence of ammonium acetate, since the highly ionized salt would repress the slight ionization of the weak acid and base. In order to see the method of evaluating this constant from the ionization constants involved, multiply both numerator and denominator by the product $(H^+)(OH^-)$, and on rearranging, we have

$$\frac{(NH_4OH)\;\;(H^+)(OH^-)\;\;(HAc)}{(NH_4^+)(OH^-)\;\;(H^+)(Ac^-)} = \frac{K_w}{K_aK_b} = K_h.$$

Denoting as before the salt concentration by C and the fraction hydrolyzed by h (and dropping out the ion product of water in both numerator and denominator, since this was introduced only to make clear the method of evaluating the constant K_h), we may substitute for (NH_4OH) its equivalent hC, for (HAc) its equivalent hC (the chemical equation shows that acid and base are formed in equal quantities), and for the ion concentrations $(1 - h)C\gamma$, and we obtain the expression

$$\frac{hC\;\;hC}{(1-h)C\gamma\cdot(1-h)C\gamma} = \frac{K_w}{K_aK_b} = \frac{h^2}{(1-h)^2\gamma^2}. \tag{8}$$

This equation shows that the fraction hydrolyzed is independent of the concentration of the salt when both acid and base are slightly ionized, except in so far as ionization of the salt changes with its concentration, which is hardly more than the deviation of the ions from the laws of ideal solutes. It is therefore safe to state that the degree of hydrolysis of a salt of a weak acid and a weak base is independent of the concentration of the salt. This is not the case for salts of a strong base or of a strong acid. Equation (8) shows further that the fractional hydrolysis increases as the ionization constant of the acid or base involved becomes smaller. For example, ammonium acetate is about

0.5 per cent hydrolyzed at 25°; but ammonium borate and ammonium cyanide are about 40 per cent hydrolyzed.

The fourth possible case is that of a salt of a strong base and a strong acid; but in this case no hydrolysis takes place. It will be noticed that hydrolysis is the reverse of the process of neutralization; and since this latter is known to take place completely for equivalent quantities of a strong acid and a strong base, it is clear that the reverse process does not take place at all. Similarly, since salts of weak acids and weak bases are hydrolyzed, the reverse process of neutralization does not take place completely when equivalent quantities of acid and base are brought together; since it is a necessary condition of chemical equilibrium that the concentration ratios at equilibrium are independent of the direction from which equilibrium was approached.

It should be noted that the hydrolysis equations (6) and (8) apply only when there is no excess acid or base present; that is, they apply only to the hydrolysis of a salt when nothing is done to diminish hydrolysis. The more general equations (6*a*) and (8*a*) apply under *all* conditions, and show the way hydrolysis of a salt may be diminished by adding one of the products of hydrolysis. Caution should be observed in the use of the simpler equations (6) and (8), that they are used only under the conditions to which they specifically apply.

Hydrolysis is of great importance in biology, for the substances chiefly concerned in life processes are salts (*i.e.*, esters) of weak acids and weak bases which hydrolyze to a considerable extent. Many problems of organic chemistry are also concerned with hydrolysis or, what amounts to the same thing, incomplete neutralization.

Distribution of a Base between Two Slightly Ionized Acids.— This distribution results when a mixture of acids is treated with a quantity of base insufficient to neutralize both of them. As stated at the beginning of the chapter, it is immaterial whether we consider that the base reacts with one of the acids, and the salt is reacted upon by the other acid; or whether a straight distribution results from partial neutralization of each acid. The chemical equation may be written for some simple method of attaining equilibrium, and the equilibrium expression formulated in accordance with this equation, without regard to the actual path by which equilibrium was attained. Suppose a liter of 0.2 formal potassium nitrite is mixed with a liter of 0.2 formal acetic acid; the reaction is $KNO_2 + HAc = HNO_2 + KAc$, for which the equilibrium expression is

$$\frac{(HNO_2)(K^+)(Ac^-)}{(HAc)(K^+)(NO_2^-)} = K.$$

The potassium ion concentration which appears in both numerator and denominator of this expression may be cancelled from it. Lacking information as to the exact extent of ionization of potassium nitrite, we may assume that it ionizes to the same extent as potassium acetate without an error of more than 2 or 3 per cent. Neither of the weak acids will be ionized to an appreciable extent in the presence of the highly ionized salts. Let x be the fraction of acetic acid which reacts according to the equation. Since we have 0.2 mol of salt and 0.2 mol of acid in 2 liters, the total salt concentration is 0.1 mol per liter, and the total acid concentration is 0.1 mol per liter. The quantity of potassium acetate formed is $0.2x$, hence its concentration is $0.1x$; since nitrous acid is formed in equivalent amount according to the equation, its concentration is also $0.1x$. Similarly the concentrations of potassium nitrite and acetic acid are each $0.1(1 - x)$. Assuming each salt is ionized to the extent γ, the acetate ion concentration is $0.1\gamma x$, and the nitrite ion concentration is $0.1\gamma(1 - x)$. Substituting these quantities in the equilibrium expression, we have

$$\frac{(0.1x)(0.1\gamma x)}{0.1(1 - x)\,[0.1(1 - x)\gamma x]} = K = \frac{x^2}{(1 - x)^2}$$

This latter form of the mass action expression applies only when the acid and salt are present in equivalent quantity, since only then will the concentrations cancel out of the equation; but the expression

$$\frac{(HNO_2)(Ac^-)}{(HAc)(NO_2^-)} = K,$$

as first formulated for this chemical reaction applies regardless of the relative quantities of salt and acid first mixed. As a means of obtaining the numerical value of K for this type of equilibrium, it should be noted that the same expression may be obtained by dividing the ionization expression for acetic acid by that for nitrous acid (cancelling the hydrogen ion concentrations, which must be the same when the two acids are present in the same solution), and that the equilibrium may therefore be written

$$\frac{x^2}{(1-x)^2} = K = \frac{K_{\mathrm{HAc}}}{K_{\mathrm{HNO_2}}}. \qquad (9)$$

In a solution containing one equivalent of base to one equivalent of each of two acids, the quantities of the two acids combined with the base are to each other as the square roots of their ionization constants, *i.e.*,

$$\frac{x}{1-x} = \sqrt{\frac{K_{\mathrm{HAc}}}{K_{\mathrm{HNO_2}}}}.$$

A similar calculation can of course be made for the distribution of an acid between two bases; the chemical equation should first be formulated, then the equilibrium expression, and finally all of the concentrations should be expressed in terms of a single unknown quantity, such as the fraction of acid combined with one base.

When the acid and the salt reacting with it are not present at the same concentration, the equilibrium may be formulated as follows: Let C_a be the total acid concentration and C_s the total salt concentration in the mixture, and let the reaction be KA + HA′ = HA + KA′, for which the equilibrium expression is

$$\frac{(\mathrm{HA})(\mathrm{A}'^-)}{(\mathrm{HA}')(\mathrm{A}^-)} = K = \frac{K_{\mathrm{HA}'}}{K_{\mathrm{HA}}}.$$

As before, we may consider that the ionization of each weak acid in the presence of its salt is negligible, and that the two salts are ionized to practically the same extent. Since the two salts have the positive ion in common, it will be recalled that it is this common ion concentration that governs the extent of ionization, not the concentration of the ion peculiar to each salt. If y is the fraction of HA′ which has reacted with KA, yC_a is the concentration of HA, and also of KA′, which is formed in equal amount as shown by the equation. The concentration of unchanged HA′ is $C_a(1 - y)$, and the concentration of unchanged salt KA is $(C_s - yC_a)$. Substituting in the expression above,

$$\frac{(yC_a)(yC_a\gamma)}{C_a(1-y)[(C_s - yC_a)\gamma]} = K = \frac{y^2C_a}{(1-y)(C_s-yC_a)}. \qquad (10)$$

It will be seen that when the acid concentration and salt concentration are equal, this equation reduces to the simpler one first derived.

By means of these relations, the ionization constant of one acid may be determined from the ionization constant of another acid, provided there is a ready method of determining the equilibrium conditions. Such a method is not always easy, however, as it must be one which determines the concentration of some one substance (from which the concentrations of the others may be computed) without disturbing the equilibrium. Thus a titration of the solution will show only the total acid and give no indication of how much of each acid is present; the precipitation of an insoluble salt of one of the acids would remove both the acid and the salt without giving any indication of the proportion of each. If one of the acids formed is volatile, a determination of its pressure above the solution fixes its concentration in the solution; if one of them is only slightly soluble, its concentration may be kept constant by keeping the solution saturated with it during the experiment. A sample of the equilibrium mixture may then be titrated for total acid, the amount of the slightly soluble one present at equilibrium is known from previous determinations of its solubility, and the concentration of the other acid may be obtained by difference. If one of the acids is soluble in benzene and the other acid is not, the first acid concentration in the equilibrium mixture may be determined by distribution experiments, in the way explained on page 117.

Indicators.—By reference to the equation showing the distribution of a base between two acids present in equivalent quantity (equation 9, page 242), it will be seen that when one of the acids is much stronger than the other (*i.e.*, has a much larger ionization constant), the stronger acid is largely neutralized when the weaker acid is still largely uncombined. Let us calculate, as an example, the fraction of hydrocyanic acid freed from potassium cyanide by the addition of an equivalent quantity of acetic acid, which is a much stronger acid. If c is the total salt concentration and x is the fraction of hydrocyanic acid liberated by acetic acid, according to the reaction KCN + HAc = KAc + HCN, the equilibrium expression is

$$\frac{(\mathrm{Ac}^-)(\mathrm{HCN})}{(\mathrm{CN}^-)(\mathrm{HAc})} = \frac{cx \cdot cx}{c(1-x)c(1-x)} = \frac{K_{\mathrm{HAc}}}{K_{\mathrm{HCN}}} = K$$

or

$$\frac{x}{1-x} = \sqrt{\frac{K_{\mathrm{HAc}}}{K_{\mathrm{HCN}}}} = \sqrt{\frac{18 \times 10^{-6}}{7 \times 10^{-10}}} = 160,$$

whence x is 0.994. Since this is the same equilibrium state as that obtained by adding a mol of potassium hydroxide to a solution containing a mol of free acetic acid and one of free hydrocyanic acid, it will be seen that practically all of the acetic acid is neutralized, and only a small fraction of hydrocyanic acid reacts.

Now suppose hydrocyanic acid to be replaced by some other acid which is as weak, but which changes color upon being neutralized. When one mol of base has been added, practically all of the acetic acid is neutralized, and only a very small portion of the other acid. Addition of more base causes the weaker acid to react, with an accompanying color change. Thus the weaker acid may be made to serve as an indicator for titrating the stronger acid.

Further study of the distribution of a base between two acids shows that when one acid is present in greater quantity than the other, a greater fraction of it is neutralized than when both acids are present in equivalent concentration. This is the case in an ordinary titration, where the quantity of weak (indicator) acid is much smaller than that of the strong acid being titrated, and hence there is practically no indicator neutralized until substantially all of the strong acid is combined with base.

Let us define an indicator as a *weak acid which changes its color upon neutralization.* This definition is all that is needed to understand the behavior of an indicator so far as analytical chemistry is concerned. An indicator is a weak acid which changes its color when neutralized, with the reverse change of color when it is freed from its salt by a strong acid, of course. However, in view of known relations between the color of organic compounds and their structure, it is necessary that some change in the structure of the complex organic radical take place at the same time as neutralization, such as a rearrangement of its atoms or a change in their linkages. Isomers such as are here concerned are called tautomeric compounds, since they change from one form to another. It is necessary that this change take place immediately upon neutralization of the indicator acid, however, and substances which change color slowly are quite unsuitable for use as indicators. In a very full and detailed discussion of indicators, Noyes[1] considers an indicator as a mixture of two tautomeric acids, HIn′ and HIn″, of which the former is a much weaker acid than the latter. Of course both of the indicator acids are very weak compared to any acid which is being titrated. The weaker acid HIn′ exists in much larger proportion in acid solutions, and its color determines the "acid color" of the indicator; but upon neutralization, the salt of the stronger acid HIn″ is formed in predominating quantity, and its color determines the "alkaline color" of the indicator. This explains the organic structural side of indicators, since the two groups In′ and In″ have different structures; but it is of more importance in the present discussion to remember that an indicator acts like a weak acid which changes color upon neutralization; therefore that the indicator acid appears to be of one color, and the indicator salt, or its ion, appears to be of another color.

It seems to be an established fact that the color change of an indicator is the result of some structural rearrangement of its molecule,[2] and that it is not due to association of it into larger molecules, or to any colloidal effect.

The color of a solution of these two tautomeric substances is determined by the relative quantities of them present. As one form predominates in acid solution and the other when the indicator acid has been neutralized, the color is determined by the *fraction* of the indicator which has been changed into its salt. The fraction of an indicator which shows the alkaline color is approximately the fraction of it which exists in the ionized form, since at the small indicator concentrations ordinarily used the salt is practically completely ionized. In the presence of its salt, or in the presence of free strong acid (one or the other is always present), the indicator acid is not appreciably ionized.

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[1] *J. Am. Chem. Soc.*, **32**, 815 (1910); see also Salm, *Z. physik. Chem.*, **57**, 471 (1906); Rosenstein, *J. Am. Chem. Soc.*, **34**, 1,117 (1912); **35**, 1,883 (1913).

[2] Lifschitz and Beck, *Kolloide-Ztsch.*, **26**, 58 (1920); Birge and Acree, *J. Am. Chem. Soc.*, **41**, 1,031 (1919); Sorensen, *Biochem. Z.*, **21**, 131 (1909).

In titrations the indicator-acid concentration is very small compared to that of the acid being titrated, and no correction need be applied for the quantity of base acting upon the indicator. As stated above, the endpoint of a titration as shown by color changes depends upon the relative quantities of indicator acid and indicator salt present in solution. The reaction

$$\mathrm{HIn} + \mathrm{KOH} = \mathrm{H_2O} + \mathrm{KIn}$$

takes place to a certain extent (HIn here including both forms of the indicator so far as structure is concerned); let x be the fraction of indicator converted to its alkaline color, *i.e.* the fraction of it neutralized, and let K_i be the ionization constant of the indicator acid. Then

$$\frac{(\mathrm{H}^+)(\mathrm{In}^-)}{(\mathrm{HIn})} = K_i,$$

but the concentration of indicator ion (In^-) is x times the total concentration of indicator added, and the remaining indicator acid is $(1 - x)$ times the indicator concentration. This indicator concentration is commonly not measured, and need not be known, since $(\mathrm{In}^-)/(\mathrm{HIn}) = x/(1 - x)$. Substituting this ratio in the ionization equation above, we have

$$\frac{(\mathrm{H}^+)x}{(1 - x)} = K_i; \quad \text{or} \quad (\mathrm{H}^+) = K_i\frac{(1 - x)}{x}. \tag{11}$$

It has been determined, by adding base to solutions containing known quantities of indicator and no other acid, that some indicators change color when only a small fraction has been neutralized, others not until nearly the whole indicator acid has been changed to its salt. Thus phenolphthalein changes its color when x is about one-tenth; methyl orange when nine-tenths of it is neutralized, rosolic acid changes when about one-tenth is neutralized. Since the indicator constants, K_i, are known for these indicators,[1] the hydrogen ion concentration at the end point may be calculated for each one. For example, K_i is 10^{-10} for phenolphthalein, the color changes when x, the fraction neutralized, is about 0.1, and upon substituting in equation (11)

$$(\mathrm{H}^+) = 10^{-10}\frac{0.9}{0.1} = 10^{-9}.$$

Similarly for rosolic acid, ($K_i = 4 \times 10^{-8}$),

$$(\mathrm{H}^+) = 4 \times 10^{-8}\frac{0.9}{0.1} = 4 \times 10^{-7}$$

and for methyl orange ($K_i = 5 \times 10^{-4}$),

$$(\mathrm{H}^+) = 5 \times 10^{-4}\ \frac{0.1}{0.9} = 5 \times 10^{-5}.$$

Since only one significant figure is known for the indicator constant, results of calculation should be rounded off in the way just illustrated. Thus, to write $(\mathrm{H}^+) = 3.6 \times 10^{-7}$ for rosolic acid is not proper, for this indicates that the actual hydrogen ion concentration is known to be between 3.5 and 3.7×10^{-7}, and such a statement is not justified by experiment.

Since rosolic acid changes color at the hydrogen ion concentration which exists in pure water, it shows the point at which a solution is really neutral. It does not follow, however, that this indicator is on that account suited to a given titration. In analytical chemistry, calculations are based upon the assumption that the acid in a solution is equivalent to the standard base added to it; and this will not be the case in a truly neutral solution if the salt formed is hydrolyzed. In titrating acetic acid, a proper end point is that at which the acid in solution is exactly equivalent to the base added; that is, the end point should come at the hydrogen ion concentration which exists in potassium acetate solution. From equation (6), page 238,

$$\frac{h^2C}{(1-h)\gamma} = \frac{K_w}{K_a} = \frac{10^{-14}}{18 \times 10^{-6}}$$

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[1] Data for other indicators may be obtained from Salm, *Biochem. Zeit.*, **21**, 131 (1909); Rupp and Loose, *Berichte*, **41**, 3,905 (1908); Jones, *J. Am. Chem. Soc.*, **37**, 776, 1,694 (1915); Tizard, *Brit. Assoc. Rept.*, **1911**, **268**; Prideaux, "Theory of Indicators," page 137.

whence, if the salt at the end point is 0.1 normal, h is 7×10^{-5}, and the concentration of free hydroxide is hC, or 7×10^{-6}. The hydrogen ion concentration may be calculated by dividing this hydroxide ion concentration into 10^{-14}, the ion product for water, and is 1.4×10^{-9}. Thus, the solution is alkaline at the end point, if this occurs when acid and base are present in equivalent quantity, and phenolphthalein, which changes color at a hydrogen ion concentration of 10^{-9} is much better for this titration than an indicator which shows true neutrality.

Suppose it is desired to titrate ammonia, a base whose ionization constant is 18×10^{-6}. Application of equation (7) for the hydrolysis of its salt leads to $h = 7 \times 10^{-5}$, or a concentration of free acid (hydrochloric acid if ammonium chloride is considered) of 7×10^{-6} for 0.1 normal salt solution. There will be this same concentration of free base as well, but in the presence of a large quantity of ammonium salt, it does not ionize appreciably. The strong acid at this concentration is however largely ionized, and for this rough calculation may be assumed completely ionized. Thus an indicator which changes color when the hydrogen ion concentration is 7×10^{-6} shows the true end point; methyl orange is suitable.

Rosolic acid, which indicates true neutrality in a solution, is less suited to either of these titrations. When it changes color, the hydrogen ion concentration (and the hydroxide ion concentration as well) is 10^{-7}. Thus in the case of ammonia, since

$$\frac{(NH_4^+)(OH^-)}{(NH_4OH)} = 18 \times 10^{-6}$$

in any solution containing these ions, by inserting 10^{-7} for the hydroxide ion concentration, it follows that $(NH_4^+)/(NH_4OH)$ is 180, and therefore there remains 1/181 of ammonium hydroxide still to be titrated when this indicator shows an end of the titration; leading to an error of about 0.5 per cent.

If phenolphthalein is used in titrating ammonia with hydrochloric acid, a very serious error results. For when this indicator changes color, the hydrogen ion concentration is 10^{-9}, hence the hydroxide ion concentration is 10^{-5}, whence

$$\frac{(NH_4^+) \times 10^{-5}}{(NH_4OH)} = 18 \times 10^{-6}, \quad \text{or} \quad \frac{(NH_4^+)}{(NH_4OH)} = 1.8,$$

which shows that only about two-thirds of the base has been titrated. A similar error would result in titrating acetic acid with methyl orange. Thus, we see that it is necessary to select a proper indicator when weak acids or weak bases are involved. For such a titration as nitric or sulfuric acid with sodium hydroxide, where there is no appreciable hydrolysis of the salt formed, and any indicator will give reliable results.

Titration of Dibasic Acids and Their Salts.[1]—Let us consider as an example the titration of a mixture of sodium carbonate and sodium bicarbonate. Phenolphthalein is commonly considered to show the point at which all normal carbonate has been converted to bicarbonate, while the bicarbonate originally present in solution is unchanged.

In the titration of soda ash, the end point is commonly taken as the point where the pink color disappears completely. Under laboratory conditions the color of phenolphthalein becomes invisible when about 3 per cent of it remains in the colored (salt) form; and since K_i is 10^{-10} and x is 0.03, $(\mathrm{H}^+) = K_i . x/(1 - x) = 3 \times 10^{-9}$. Upon substituting this hydrogen ion concentration into the ionization expressions for carbonic acid it is found that

$$\frac{(\mathrm{HCO_3^-})}{(\mathrm{H_2CO_3})} = 120 \quad \text{and} \quad \frac{(\mathrm{CO_3^{--}})}{(\mathrm{HCO_3^-})} = 0.013$$

This means that about 1 per cent of the carbonate is still to be titrated, and that about 1 per cent of the bicarbonate has been changed to free carbonic acid when the pink color disappears. As the first of these errors corresponds to the use of too little standard acid, and the second to the use of acid where none should have been used, the *net error* of the two processes is quite small, and the common analytical procedure leads to a correct end point.

Change of Chemical Equilibrium with Temperature.—When any chemical system at equilibrium is heated, the chemical reaction proceeds in the direction which absorbs heat. For example, neutralization of an acid by a base evolves heat, hydrolysis (the reverse process) absorbs heat; hence when a salt solution is heated the fraction hydrolyzed increases. Similarly the union of hydrogen and oxygen to form water vapor, the union of carbon monoxide and oxygen to form carbon dioxide, and the union of hydrogen atoms into molecules all evolve large quantities of heat. Heat would therefore be required to tear these molecules apart, and an increase of temperature (*i.e.*, absorption of heat by the system at equilibrium) is attended by an increase in the fraction dissociated. Table 90 shows this effect at 1 atmosphere pressure.

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[1] In this connection, read again the paragraph on ionization of dibasic acids, page 232.

TABLE 90.—PERCENTAGE DISSOCIATION OF GASES[1]

T_{abs}	H_2O	CO_2	H_2
1,000	0.000028	0.0002	
1,200	0.000745	0.0093	
1,400	0.00787	0.146	
1,600	0.0446	0.110	
1,800	0.1700	0.546	
1,900	0.302	1.04	
2,000	0.504	1.84	0.33
2,200	1.21	5.0	0.92
2,500	3.38	15.6	3.15
3,000	11.1	48.5	13.
3,500	....	....	34.
4,000	....	....	61.

There is a quantitative relation between the heat of a reaction and the change of its equilibrium constant with temperature. Before giving this equation, it is necessary to mention again the convention followed in writing expressions for chemical equilibrium. First the chemical reaction should be written down, the appropriate heat term corresponding to it should be added to this chemical equation, then the equilibrium expression should be written with the products of the reaction in the numerator. It is of course permissible to write the chemical reaction in either way; thus $2H_1 = H_2 + 90{,}000$ cal., or $H_2 = 2H_1 - 90{,}000$ cal., provided the equilibrium expression is written $\frac{p_{H_2}}{p^2_{H_1}} = K$ to correspond to the first way of writing the chemical equation, and $p^2_{H_1}/p_{H_2} = K'$ if the chemical reaction is written in the second way. Corresponding to the first way, Q, the heat of reaction is

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[1] Langmuir, *J. Am. Chem. Soc.*, **28**, 1,357 (1906); **37**, 417 (1915).

+90,000 cal., and for the second way Q' is −90,000 cal. Then the change of equilibrium constant with temperature is shown by the differential equation[1]

$$\frac{d \ln K}{dT} = \frac{-Q}{RT^2} \tag{12}$$

which is called the van't Hoff equation. By means of this equation the equilibrium constant at any temperature can be calculated from that at another temperature if the heat of the chemical reaction is known, or the heat of reaction may be calculated from equilibrium constants at two different temperatures, provided Q, the heat evolved during chemical reaction, does not change appreciably over the temperature interval involved. This equation may be integrated between limits, and becomes

$$2.303 \log \frac{K_2}{K_1} = \frac{-Q}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{13}$$

where 2.303 is the conversion factor from natural to ordinary logarithms. In using this equation, R is expressed in calories if the heat of reaction is so expressed. Since the equilibrium constants appear in this equation as a ratio, any units may be used in formulating them, provided the same units are employed at both temperatures. Thus if the partial pressures are in millimeters of mercury in one case, they must be in the other also.

Let x be the fractional dissociation of hydrogen into atoms at 3,000° absolute; for each mol of hydrogen composing the equilibrium mixture at a low temperature, x mols dissociate at 3,000°, forming $2x$ mols of H_1, and there remain $(1 - x)$ mols of H_2. Then the mol fraction of H_1 is $2x/(1 + x)$, where $(1 + x)$ is $1 - x + 2x$, or the total mols of gas; and the mol fraction of H_2 is $(1 - x)/(1 + x)$. When the total pressure is 1 atmosphere, the partial pressures in atmospheres are equal to the mol fractions, and, considering the chemical reaction as $2H_1 = H_2 + 90{,}000$ cal., we have

$$\frac{(1 - x)/(1 + x)}{(2x)^2/(1 + x)^2} = K = \frac{1 - x^2}{4x^2}.$$

At 3,000° hydrogen is 13 per cent dissociated, hence x is 0.13

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[1] As in other cases, *ln* is here used to indicate natural logarithms; those to the base 10 are indicated by the abbreviation *log*.

and K is 14.5. It is desired to calculate the equilibrium constant at 3,500° on the absolute scale, and from it the fractional dissociation into atoms at this temperature. Substitute 14.5 for K_2 and 3,000° for T_2 in equation (13), put 3,500° for T_1 and solve for K_1,

$$2.3 \log \frac{14.5}{K_1} = \frac{-90,000}{1.99}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

whence K_1 is 1.7. Upon equating K_1 to $(1 - x)^2/4x^2$, the fractional dissociation at 3,500° is 0.36 or 36 per cent. The experimental value is 34 per cent. This deviation is due to our assumption that Q, the heat of this reaction, remains constant over the temperature range 3,000 to 3,500°, which is not quite the case. It would be better to express Q as a function of the temperature as was explained on page 209, and substitute this expression into equation (12) before integrating it between temperature limits, but the change of Q with temperature is not serious in this case.

Let us consider an equilibrium in which the heat of reaction changes considerably with the temperature, namely $2CO_2 = 2CO + O_2 - 136,000$ cal. at 20°. From equation (7), page 210, $dQ = -\Delta C_p dT$. The heat capacity of carbon dioxide may be taken as $7.0 + 0.0028T$ calories per mol, that for carbon monoxide and oxygen $6.5 + 0.001T$ calories per mol. Then the increase in heat capacity, ΔC_p, is $3(6.5 + 0.001T) - 2(7.0 + 0.0028T)$, or $\Delta C_p = 5.5 - 0.0026T$. Substituting in the equation above, and integrating,

$$Q = -5.5T + 0.0013T^2 + I,$$

where I is an integration constant. When T is 293 (*i.e.*, at 20°C.), Q is $-136,000$, whence the integration constant is $-134,500$, and the value of $-Q$ to be inserted in van't Hoff's equation is $134,500 + 5.5T - 0.0013T^2$. Then

$$d \ln K = \left(\frac{134,500 + 5.5\,T - 0.0013T^2}{RT^2}\right) dT$$

and, upon integration, since R is 1.99 cal.,

$$\ln \frac{K_2}{K_1} = 67,600\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + 2.8 \ln \frac{T_2}{T_1} - 0.0007(T_2 - T_1).$$

Suppose it is desired to calculate the equilibrium constant at 2500° from that at 2200°; by inserting these temperatures in the above equation, converting to ordinary logarithms and solving, we find that $\frac{K_{2500}}{K_{2200}}$ is 46.

Let x be the fractional dissociation. Then for two mols of CO_2 in the system at room temperature, there will be $2x$ mols dissociated at the temperature T, hence $2x$ mols of carbon monoxide formed, x mols of oxygen, and $2 - 2x$ mols of carbon dioxide remaining. The total number of mols is $2x + x + (2 - 2x)$ or $2 + x$, and the partial pressures when the total pressure is 1 atmosphere are therefore $2x/(2 + x)$ for carbon monoxide, $x/(2+x)$ for oxygen, and $(2 - 2x)/(2 + x)$ for carbon dioxide. The equilibrium expression corresponding to $2CO_2 = 2CO + O_2$ is

$$K = \frac{p_{CO}^2 \cdot p_{O_2}}{p_{CO_2}^2} = \frac{\left(\frac{2x}{2+x}\right)^2 \frac{x}{(2+x)}}{\left(\frac{2-2x}{2+x}\right)^2} = \frac{4x^3}{(2-2x)^2(2+x)}.$$

At 2200°, x is 0.05, whence K_{2200} is 67×10^{-6}; by the calculation above, K_{2500} is 46 times this, or 3150×10^{-6}. Then upon solving the equation

$$K_{2500} = \frac{4x^3}{(2-2x)^2(2+x)} = 3150 \times 10^{-6},$$

the fractional dissociation of carbon dioxide at 2500° absolute is obtained. It is not necessary to apply a general solution for cubics to this problem however. By estimating values of x and substituting them into the equation it is found that $x = 0.16$ gives a smaller value to the left hand side than $3{,}150 \times 10^{-6}$ while $x = 0.17$ gives a larger value. The dissociation is therefore about 16 per cent: direct experiment gives 15.6 per cent.

In case the temperature range over which a calculation is to be made is small, the heat of reaction may be assumed constant, thus avoiding the extra calculation involved in the case just explained. It should be remembered however, that in many cases the heat of a reaction at two different temperatures is quite different, and that calculations assuming it constant are liable to be in error.

For approximate calculations it is sometimes sufficient to calculate the heat of a reaction at each of the two temperatures involved in a calculation, assume that the average of these two values is a sufficient representation of Q over the whole range, and employ the simple integrated van't Hoff equation (11). But the van't Hoff equation should not be applied over a range of temperature such that some of the substances involved are vapors at the higher temperature and liquids or solids at the lower temperature. Under these conditions the heat of reaction Q undergoes a sudden change with temperature which cannot be represented by a simple equation.

Questions

1. When a mixture of one mol of HCl and 0.48 mols of oxygen is brought to equilibrium according to the Deacon process reaction $4HCl + O_2 = 2H_2O + 2Cl_2$ at 386°, it is found that 0.402 mols of chlorine have been formed. Calculate the partial pressure of each gas in the equilibrium mixture when the total pressure is 1 atmosphere, and calculate the equilibrium constant. Ans. $K = 80$.

2. From the data of the previous problem, calculate the yield of chlorine when a mol of HCl and a mol of oxygen are heated to equilibrium at 386°. (Formulate the partial pressures in terms of x, the fraction of HCl oxidized to chlorine, and solve the resulting equation by trial).

3. The equilibrium constant of the Deacon process reaction is 80 at 386° and 296 at 352°. Calculate how much heat is evolved by the reaction per mol of chlorine produced. Calculate the equilibrium constant at 419°. Ans. $K = 33.2$.

4. Potassium cyanide is 3.6 per cent hydrolyzed in 0.1 formal solution at 50°. Calculate the ionization constant of water at this temperature. The ionization constant of hydrocyanic acid is 7×10^{-10}.

5. Phosgene is 80 per cent dissociated into carbon monoxide and chlorine at 550° and 91 per cent dissociated at 600°. Calculate the heat of dissociation, and make clear whether heat is evolved or absorbed upon dissociation.

6. When a mol of hydrogen dissociates at 3,000° absolute, 90,000 cal. of heat are absorbed. Calculate the fractional dissociation at 2,200° from the fact that at 3,000° hydrogen is 13 per cent dissociated into atoms. Assume a constant heat of reaction.

7. The equilibrium constant of the reaction $CO_2 + H_2 = CO + H_2O$ is 1.2 at 886°C. and 1.59 at 986°. Calculate the heat of this reaction, assuming it to be constant over the whole temperature range. From this heat of reaction, calculate the equilibrium constant at 786° or at 1,086°. The measured constant at 1,086 is 1.96, and at 786 it is 0.84.

8. A small amount of phenolphthalein is added to a solution prepared by mixing 20 c.c. of 0.1 normal NH_4Cl with 3 c.c. of 0.1 normal NH_4OH. Calculate the hydrogen ion concentration in solution, and the fraction of the indicator transformed to the pink form. $K_i = 10^{-10}$.

9. A solution 0.1 formal in phosphoric acid is titrated with NaOH, using methyl orange as indicator, and the end point is taken when 91 per cent of the

indicator shows the alkaline color. The ionization constants of H_3PO_4 are $K_1 = 10^{-3}$, $K_2 = 2 \times 10^{-7}$, $K_3 = 3.6 \times 10^{-13}$. (*a*) Calculate the hydrogen ion concentration at the end point. (*b*) Calculate what fraction of the acid has been converted into NaH_2PO_4. (*c*) What fraction has been converted into Na_2HPO_4?

10. The 0.1 formal H_3PO_4 is titrated with NaOH, using phenolphthalein as indicator, and the end point is taken when 5 per cent of the indicator is changed to pink. (*a*) Calculate (H^+), the ratio $(H_2PO_4^-)/(HPO_4^{=})$ and the ratio $(HPO_4^{=})/(PO_4^{---})$ corresponding to this end point. How much NaOH (0.10 normal) would be required for the titration?

11. To 100 c.c. of 0.1 normal sodium acetate at 25° is added 0.244 grams of benzoic acid. The ionization constant of acetic acid is 18×10^{-6}, that for benzoic acid is 60×10^{-6}. Calculate the fraction of base combined with each acid at equilibrium.

12. The equilibrium constant of the reaction $2SO_3 = 2SO_2 + O_2$ at 527° is 15.5×10^{-6} and at 627° it is 3.16×10^{-4}. Calculate the heat of the reaction. Calculate the equilibrium constant at 727°.

13. To a solution 0.1 formal in KNO_2 and 0.1 formal in KAc is added an equal volume of 0.1 formal HCl. Calculate the concentration of each free acid.

14. Calculate the hydrolysis of 0.1 formal ammonium formate at 25°.

15. If a liter of 0.1 formal ammonium formate is added to a liter of 0.1 formal acetic acid, what fraction of the salt will be converted to NH_4Ac? What will be the fraction converted to acetate when a liter of each of these solutions is added to three liters of water?

16. At 3,000° (absolute) hydrogen is 13 per cent dissociated into its atoms when the total pressure is 1 atm. Calculate the partial pressure of the atoms and of the molecules, and from these pressures calculate the equilibrium constant. Calculate the total pressure at which the degree of dissociation would be 10 per cent at 3,000° absolute.

17. When one gram of water is placed in a space of one liter at 450° in contact with liquid sulfur, the reaction $2H_2O + 3S = 2H_2S + SO_2$ takes place. From the value of the equilibrium constant given as the average in Table 84, calculate the partial pressures of each substance at equilibrium. Calculate what fraction of the water is converted into hydrogen sulfide.

18. A mixture of one mol of carbon dioxide and three mols of hydrogen is heated at 986° until equilibrium is established. Calculate the partial pressure of each gas in the equilibrium mixture. The equilibrium constant is 1.59 for the reaction $CO_2 + H_2 = H_2O + CO$.

19. Sodium phenolate is 5.6 per cent hydrolyzed at 25° in 0.03 formal solution. Calculate the hydrolysis constant and the ionization constant of phenol as an acid.

20. The sodium salt of mesitol is 13.8 per cent hydrolyzed in 0.03 formal solution. Calculate its ionization constant as an acid. If 0.01 formula weight of sodium hydroxide is added to a solution 0.01 formal in phenol and 0.01 formal in mesitol, what fraction of each acid will be neutralized?

CHAPTER IX

HETEROGENEOUS EQUILIBRIUM

We have so far considered equilibrium in a single phase, either gas or solution. In many cases, the equilibrium conditions in a given phase are closely related to those in another phase; often they are fixed completely by the presence of a solid in excess. Thus the concentration of a solution of any given temperature when it is in equilibrium with some of the solid solute is determined by the solubility of that solute.

Some examples of two-phase equilibrium have been studied in earlier chapters, where a solid present in excess fixed the concentration or pressure in a gaseous phase or in a solution. The partial pressure of a solute above a solution is fixed by its concentration in the solution (Henry's law), the vapor pressure of a solution at a fixed temperature is proportional to the mol fraction of solvent (Raoult's law), the concentration of solute in one liquid phase fixes that in another liquid in equilibrium with it (distribution law), and the equilibrium between a solution and solid solvent is established according to the freezing point laws. This chapter is mainly concerned with similar aspects of equilibrium when more than one phase is present.

Solids and Gases.—When gases react with a solid to produce other solids and gases, the equilibrium is formulated (after writing the chemical reaction) in the same way as for other equilibria, except that the partial pressures (or concentrations) of solid substances are left out entirely. This is equivalent to including all of these partial pressures in the numerical value of the equilibrium constant, and allows the formulation of equilibria when these partial pressures (sublimation pressures) are not capable of determination. Thus in the reaction

$$Ag_2S \text{ (solid)} + H_2 = 2Ag \text{ (solid)} + H_2S,$$

it is not necessary to write

$$\frac{p^2_{Ag}\, p_{H_2S}}{p_{Ag_2S}\, p_{H_2}} = K',$$

for the sublimation pressures of these solids are too small for experimental determination. In the presence of each solid, the partial pressure of it above the solid is constant so long as the temperature remains constant, and we may therefore write $\frac{p_{H_2S}}{p_{H_2}} = K$ to represent this equilibrium, where K is the product of K' and the ratio of two constant sublimation pressures for silver and silver sulfide, *i.e.*, $K = K' \frac{p_{Ag_2S}}{p^2_{Ag}}$. Indeed it has not been established that there is any silver or silver sulfide present in the gaseous phase at all, but experiment shows that when silver sulfide and hydrogen are brought together at any temperature, the ratio of the partial pressure of hydrogen sulfide to hydrogen is constant at equilibrium in the presence of both solids, regardless of the quantities of each employed; and that this same ratio is established when silver and hydrogen sulfide are brought together in any quantity, though the quantities of the two solids remaining may be in any ratio whatever at equilibrium.

Thus at 476° the ratio of the partial pressure of hydrogen sulfide to hydrogen[1] is 0.359 at equilibrium, *provided both solid substances are present.* It is important to remember that the equilibrium ratio $p_{H_2S}/p_{H_2} = K$, while it does not contain any written reference to silver or silver sulfide, refers only to the equilibrium between *these two solids* and the two gases. If a mol of silver sulfide were put into contact with ten mols of hydrogen, there would be formed one mol of hydrogen sulfide and nine of hydrogen would remain, but no silver sulfide would be present. This condition is one of true chemical equilibrium, but it is not the equilibrium to which the constant ratio of hydrogen sulfide to hydrogen applies. The limiting ratio of the two substances in order to establish this equilibrium is one mol of hydrogen to 0.264 mols of silver sulfide, for by reaction this would produce 0.264 mols of hydrogen sulfide and 1 − 0.264 or 0.736 mols of hydrogen would remain. These mol fractions in the gas mixture are in the ratio 0.359, and any quantity of silver sulfide greater than 0.264 formula weights per mol of hydrogen would therefore suffice to establish equilibrium with all four substances present. Any smaller quantity of silver sulfide per mol of hydrogen would be completely reduced without raising the ratio p_{H_2S}/p_{H_2} to the equilibrium value for this temperature. Similarly, the least quantity of hydrogen which would suffice to reduce completely one formula weight of silver sulfide at 476° is one mol for the actual chemical process plus (1/0.359 = 2.79) mols to maintain the equilibrium ratio, or a total of 3.79 mols. If a smaller quantity of hydrogen reacts upon a formula weight of silver sulfide, equilibrium is established in the gaseous phase before all of the sulfide is reduced; if a larger quantity of hydrogen is employed, complete reaction takes place without forming enough hydrogen sulfide to produce the equilibrium ratio of partial pressures.

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[1] Keyes and Felsing, *J. Am. Chem. Soc.*, **42**, 246 (1920).

As with homogeneous equilibrium, that in which several phases are involved changes with the temperature. In the example just considered, the ratio of hydrogen sulfide to hydrogen at equilibrium is as follows:

TABLE 91.—EQUILIBRIUM CONSTANTS AT DIFFERENT TEMPERATURES

Absolute temperature	Centigrade temperature	Equilibrium constant
749	476	0.359
811	518	0.325
890	617	0.278

The van't Hoff equation may be applied to heterogeneous equilibria in the same way as to reactions taking place in a single phase, to calculate the equilibrium at one temperature from that at another when the heat of reaction is known, or to calculate the reaction heat from equilibrium constants at two different temperatures. Thus, to calculate the heat of reaction,

$$2.303 \log \frac{K_2}{K_1} = \frac{-Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

And by substituting 0.359 for K_1 and 476 + 273 for T_1; 0.278 for K_2 and 617 + 273 for T_2, we find that $-Q = -2{,}410$ cal., or

$$Ag_2S \text{ (solid)} + H_2 = 2Ag \text{ (solid)} + H_2S + 2{,}410 \text{ cal.}$$

Dissociation Pressures.—When a solid decomposes to form another solid and a gas, the equilibrium constant of the reaction is the pressure of the gas. Thus for the reaction

$$CaCO_3 \text{ (solid)} = CaO \text{ (solid)} + CO_2,$$

the equilibrium expression is $p_{CO_2} = K$.

In many cases a solid upon decomposition forms two or more gases; for example

$$NH_4Br \text{ (solid)} = NH_3 + HBr + NH_4Br$$

for which the mass-action expression is $p_{NH_3} \cdot p_{HBr} = K$. As usual, the partial pressure of ammonium bromide is included in the value of K for the temperature in question. In some cases, such as ammonium hydrogen sulfide, NH_4HS, complete dissociation occurs in the vapor phase, in which case each partial pressure is half of the total dissociation pressure. In cases such as that of ammonium bromide, dissociation is incomplete, and the extent of this dissociation must be determined from vapor density measurements or in some other suitable way. From the change of equilibrium with temperature the heat effect of the reaction can be computed in the same way as for homogeneous equilibrium. The heat effect so computed is the heat of the complete reaction NH_4Br (solid) $= NH_3 + HBr + Q$; not the effect which would be observed if a formula weight of solid salt at the temperature in question were allowed to undergo the incomplete reaction corresponding to equilibrium. This same statement of course applies to any change of equilibrium with temperature computed from the van't Hoff equation. Table 92 shows some experimental results. It will be noted that the equilibrium constant changes rapidly as the temperature increases.

TABLE 92.—DISSOCIATION PRESSURES OF AMMONIUM BROMIDE

Temperature	Pressure $NH_3 = HBr$, mm.	Pressure NH_4Br mm.	Total pressure mm.	Per cent dissociated	$K = pNH_3pHBr$
320	28.5	43.6	100.6	39.3	812
330	34.6	65.5	134.7	34.9	1,200
340	42.0	94.8	178.8	30.6	1,765
350	49.4	137.7	236.6	26.3	2,440
360	55.7	199.	310.4	22.0	3,100
370	61.0	282.9	404.8	17.7	3,720
380	62.0	400.5	525.5	13.4	3,840

Smith and Lombard, *J. Am. Chem. Soc.*, **37**, 38 (1915).

Two interesting phenomena are here taking place side by side; an increase in the vapor pressure of solid ammonium bromide, and a tendency toward increased dissociation at higher temperatures. The former of these effects largely increases the total pressure; but an increase of total pressure drives back the dissociation to such an extent that there is a decrease in fractional dissociation of *saturated* ammonium bromide vapor with increasing temperatures. For a constant total pressure there would be an increased dissociation at higher temperatures, as in the case of other dissociation reactions.

Distribution Between Two Liquids.—The case in which a solute has the same molecular weight in both solvents has been described on page 119, where it was seen that the ratio of the concentration in one liquid to that in the other was constant. In many cases there is a dissociation into simpler molecules upon passage from one solvent to another, and the simple distribution ratio does not apply. For example, benzoic acid exists in water as single molecules which are not ionized to any great extent, and in benzene it is almost entirely associated into double molecules, $(C_6H_5COOH)_2$. Passage from one phase to the other is attended by a chemical reaction, the equation for which is

$$2\ C_6H_5COOH = (C_6H_5COOH)_2;$$

accordingly the equilibrium is shown by the relation

$$\frac{C_{\text{benzol}}}{C^2_{\text{water}}} = K.$$

The following table shows that this method of formulation

TABLE 93.—DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 20°

Molal concentration		C_b/C_w	C_b/C_w^2
in water	in benzene		
0.0075	0.0084	1.12	150
0.0093	0.0131	1.41	152
0.0125	0.0239	1.92	154
0.0167	0.0437	2.62	153
0.0210	0.0651	3.10	148
0.0327	0.165	5.05	154
0.0429	0.295	6.90	160

represents the facts as determined by experiment, while the simple distribution law does not hold even approximately.

A similar behavior is shown by most organic acids when distributed between water and hydrocarbons. For example, when picric acid is distributed between water and toluene,[1] the ratio of concentrations changes from 6.6 to 14.9; but the equilibrium ratio as formulated between the concentration in toluene and the square of the concentration in water leads to a more satisfactory constant.

There are other cases in which the distribution ratio changes with the concentration of distributed solute which cannot be explained by simple association in one phase or the other; they must be added to the long list of unexplained phenomena in connection with solutions which are set down as "deviations from the laws of ideal solutes," and which should be called *failure of* the laws of ideal solutions. In such cases, the concentration in one phase may be plotted against that in the second phase from several points determined by experiment, and this empirical curve may then be used in determining other concentrations in one phase when that in the second phase is known.

Solids and Dissolved Substances.—The simplest case of equilibrium between a solid and a dissolved substance is that of a saturated solution of a substance which does not ionize upon solution, the concentration of which solution depends upon the temperature alone. For a given temperature the equilibrium expression is $C = K$, where C is the concentration of the substance. From the solubility at two temperatures not too far apart the heat of solution into the saturated solution may be calculated from van't Hoff's equation. This will not be the heat effect of solution of a mol of the substance in a large quantity of water unless its heat of dilution is very small. The equilibrium reaction is the passage of molecules of the solute from the solid state into saturated solution, and a calculation of the heat of reaction from equilibrium constants can only give the heat effect corresponding to the reaction which actually occurs. The heat effect so obtained, plus the heat effect of adding this saturated solution to a large quantity of water is equal to the heat effect of adding the same quantity of solid to a large quantity of water in the first place. (Law of constant heat summation.)

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[1] *Berichte,* **37**, 4,746 (1904).

When a slightly ionized substance such as benzoic acid is in equilibrium with its solid phase, the concentration of non-ionized molecules in the solution is constant. According to the mass-action law, the expression $(H^+)(Bz^-)/(HBz) = K$ is also true for all solutions containing these ions and molecules, where HBz is benzoic acid, and Bz is benzoate ion. Upon clearing this expression of fractions, we have $(H^+)(Bz^-) = K(HBz) =$ *const.* This is a statement of the law of solubility product, which says that in a saturated solution the product of the ion concentrations is a constant for a simple binary electrolyte, *i.e.*, one which gives one positive ion and one negative ion upon ionization. According to this law, the addition of a little nitric acid or hydrochloric acid to a solution saturated with benzoic acid should decrease the concentration of benzoate ions in solution, by forcing them to combine with hydrogen ions and form non-ionized molecules, and cause precipitation of the benzoic acid formed. But as benzoic acid in its saturated solution (0.026 formal) is only 4 per cent ionized, removal of practically all of its ions would decrease the solubility only 4 per cent. The acid would have no effect on the concentration of non-ionized molecules, hence only a small precipitation results from the addition of a strong acid in moderate amount, though the concentration of benzoate ions may be reduced to a hundredth of its former value. A small quantity of sodium benzoate would also produce this effect; it would greatly decrease the hydrogen-ion concentration, but produce only a small effect on the total quantity of benzoic acid in solution.

Solubility Product for Ionized Substances.—While the law of mass action does not apply to the ionization of strong acids and bases and salts, experiment shows that the ion-concentration product or solubility product is nearly constant for many slightly soluble salts. Highly soluble salts deviate considerably from the law of solubility product, in much the same way that these concentrated solutions deviate from the other simple laws of solutions. In accordance with the convention already adopted, the concentrations of non-ionized molecules of largely ionized substances are not included in equilibrium expressions, and the concentration of the ions is calculated from the total salt concentration and the fractional ionization as derived from conductivity ratios or from freezing point depressions. When silver acetate is dissolved in water, the reaction is AgAc (solid) = $Ag^+ + Ac^- +$ AgAc (dissolved molecules); and the equilibrium expression is $(Ag^+)(Ac^-) = K$. As this salt is highly ionized, addition of any ionized acetate to the solution decreases the solubility, since a large increase in the acetate-ion concentration must be attended by a corresponding decrease in the silver-ion concentration. This decrease is brought about through their combination with acetate ions, followed by precipitation. Table 94 shows the effect of sodium acetate upon the solubility of silver acetate. It will be observed that solubility product is fairly constant. It should not be inferred from the constant value of the solubility product that there is a constant concentration of silver acetate molecules in solution. This cannot be true unless the law of mass action applies to silver acetate, for if $(Ag^+)(Ac^-)$ is constant and (AgAc) is constant, their quotient is also constant. As a matter of fact the concentration of non-ionized molecules decreases when either sodium acetate or silver nitrate is added to the solution.

TABLE 94.—SOLUBILITY OF SILVER ACETATE AT 16°

Concentration of sodium acetate	Ionization of sodium acetate	(Ac^-)	Concentration of silver acetate	Ionization of silver acetate	Solubility product
0.000	.....	......	0.0603	0.708	18.2×10^{-4}
0.061	0.786	0.0731	0.0392	0.645	18.5×10^{-4}
0.119	0.758	0.107	0.0280	0.597	17.9×10^{-4}
0.239	0.708	0.174	0.0208	0.523	18.8×10^{-4}

Stieglitz, *J. Am. Chem. Soc.*, **30**, 946 (1908).

The solubility of thallium chloride in the presence of chlorides and of other thallium salts is shown in Table 95, where the concentration of non-ionized thallium chloride molecules in each solution is seen to change with the total salt concentration. Thus, while the solubility product is fairly constant, the salt does not conform to the mass-action law, and the concentration of non-ionized molecules in equilibrium with solid thallium chloride is not constant. The explanation for this effect is not known.

TABLE 95.—SOLUBILITY OF THALLOUS CHLORIDE AT 25° IN THE PRESENCE OF ADDED POTASSIUM CHLORIDE OR ADDED THALLOUS NITRATE

(Concentrations in mols per thousand liters)

Concentration added salt		Solubility	(Tl^+)	(Cl^-)	$(TlCl)$	K $(Tl^+)(Cl^-) = K$
$TlNO_3$	KCl					
0	...	16.07	14.32	14.32	1.755	204.9 ✓
25	...	8.80	29.17	7.405	1.395	216.0
50	...	6.24	46.87	4.99	1.248	233.9
100	...	4.22	82.05	3.13	1.093	256.8
...	25	8.69	7.30	29.88	1.390	218.1
...	50	5.90	4.70	48.85	1.204	229.6
...	100	3.96	2.90	88.40	1.061	256.3
...	200	2.68	1.74	166.5	0.94	290.0

The data are quoted from Bray, *J. Am. Chem. Soc.*, **33,** 1,674 (1911).

It will be seen from this table that equivalent solutions of a chloride and a thallous salt produce about the same decrease in solubility. Thus, a normal solution of one chloride has about the same effect as a normal solution of another chloride. This is better shown by the following table.

TABLE 96.—SOLUBILITY OF THALLOUS CHLORIDE IN THE PRESENCE OF AN ADDED SALT

(Equivalents per 1,000 liters)

Concentration of added salt	Solubility in the presence of				
	HCl	KCl	$BaCl_2$	$TlNO_3$	Tl_2SO_4
25	8.66	8.69	8.98	8.80	8.9
50	5.83	5.90	6.18	6.24	6.77
100	3.83	3.96	4.16	4.22	4.68
200	2.53	2.68	2.82	....	....

Reactions between Solids and Dissolved Substances.—Equilibrium between ferrous carbonate and dissolved carbon dioxide has been studied[1] and found to give a satisfactory equilibrium constant. The concentration of the ions of the ferrous bicarbonate is taken into consideration, and the concentration of ferrous carbonate is left out of the equilibrium expression. The chemical equation is

$$FeCO_3(\text{solid}) + H_2CO_3 = Fe(HCO_3)_2,$$

and the equilibrium expression is

$$\frac{(Fe^{++})(HCO_3^-)^2}{(H_2CO_3)} = K.$$

Let S denote the solubility of ferrous salt in the carbonic acid solutions, *i.e.*, its molal concentration in carbonic acid solution in equilibrium with solid ferrous carbonate, as determined by titration of a portion of the saturated solution, and let γ be the fractional ionization; then the molal concentration of ferrous ion will be $S\gamma$, and that of bicarbonate ions will be twice as great, or $2S\gamma$. The ionization of carbonic acid is slight, and in the presence of dissolved ferrous bicarbonate, which is highly ionized, may be neglected entirely in the calculation. Table 97 shows the results of experiments at 30°, where the equilibrium constant is

$$K = \frac{S\gamma(2S\gamma)^2}{(H_2CO_3)}.$$

In calculating the carbonic acid concentration in the denominator, that acid which reacted with ferrous carbonate was deducted from the total carbonic acid present.

TABLE 97.—SOLUBILITY OF FERROUS CARBONATE IN CARBONATED WATER

Molal concentrations at 30°		Ionization of $Fe(HCO_3)_2$	Equilibrium constant K
H_2CO_3	$FeCO_3$		
0.1985	0.00256	0.909	6.35×10^{-10}
0.2327	0.00274	0.907	6.60
0.3116	0.00304	0.902	6.60
0.3294	0.00311	0.900	6.72
0.4046	0.00332	0.896	6.53
0.6600	0.00402	0.884	6.80
0.7600	0.00434	0.878	(7.30)

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[1] Smith, *J. Am. Chem. Soc.*, **40,** 879 (1918).

The equilibrium constant is seen to increase slightly at higher concentrations, which is in accord with the behavior of most mass-action expressions involving ionized solutes. The pressure necessary to produce a concentration of carbonic acid such as that in the last line of the table is about 25 atmospheres.

It is interesting to note the various other equilibria which also exist in this system. When a system is in equilibrium, it must be so as regards all of its parts. Here the solution is saturated with the slightly soluble substance ferrous carbonate, and the solubility product must therefore be maintained; since there are carbonate and bicarbonate ions in the presence of carbonic acid, the dissociation relations required of this substance by the mass law must also be maintained. These various equilibria may be expressed by the following chemical equations and their corresponding mass-action expressions:

$$\begin{aligned} H_2CO_3 &= H^+ + HCO_3^- & K_1 &= (H^+)(HCO_3^-)/(H_2CO_3) \\ HCO_3^- &= H^+ + CO_3^{--} & K_2 &= (H^+)(CO_3^{--})/(HCO_3^-) \\ FeCO_3\ (\text{solid}) &= Fe^{++} + CO_3^{--} & K_3 &= (Fe^{++})(CO_3^{--}). \end{aligned}$$

If now we multiply together the equations for K_1 and K_3, and divide this product by K_2 we have

$$\frac{(Fe^{++})(HCO_3^-)^2}{(H_2CO_3)} = \frac{K_1K_3}{K_2} = K,$$

which is seen to be the equilibrium constant first written for this reaction. K is known from experiment, the dissociation constants K_1 and K_2 for carbonic acid at 30° are 3.7×10^{-7} and 4.9×10^{-11} respectively, whence the solubility product for ferrous carbonate is 34.5×10^{-12}. The solubility in pure water, in mols per liter, is the square root of this number, or 5.8×10^{-6}. This solubility product was of course derived from experiments in the presence of excess carbonic acid, and there was on that account no hydrolysis of the ferrous carbonate. The solubility of 5.8×10^{-6} mols per liter holds only under the assumption for which it was derived, namely in the absence of any hydrolysis.

The above example is typical of a simple investigation of chemical equilibrium, and illustrates the way in which various equilibrium constants may be combined to give the desired constant governing the equilibrium under consideration.

Conversion of One Solid into Another.—A familiar example is the conversion of barium sulfate into barium carbonate by boiling it with sodium carbonate solution in excess. The reaction is

$$BaSO_4\ (\text{solid}) + Na_2CO_3 = BaCO_3\ (\text{solid}) + Na_2SO_4,$$

and the corresponding mass-action expression is

$$(SO_4^{--})/(CO_3^{--}) = K.$$

Since the solution is saturated with both solids, the solubility product for each must be satisfied, *i.e.*, $(Ba^{++})(SO_4^{--}) = k_1$ and $(Ba^{++})(CO_3^{--}) = k_2$. When pure water is saturated with $BaSO_4$, the concentration of each ion is $S_1\gamma$, where S_1 is the formal solubility and γ is the fractional ionization; hence k_1 is $S_1^2\gamma^2$, and since the solution is so dilute that ionization is essentially complete, k_1 is practically S_1^2; similarly, k_2 for $BaCO_3$ is S_2^2. These values are

$$(Ba^{++})(CO_3^{--}) = 25 \times 10^{-10} \text{ and } (Ba^{++})(SO_4^{--}) = 10^{-10}$$

for 20°, and upon dividing the second of these by the first we obtain a value for the equilibrium constant K,

$$\frac{(SO_4^{--})}{(CO_3^{--})} = \frac{S_1^2}{S_2^2} = 1/25 = 0.04,$$

since the solubility of barium carbonate is five times that of the sulfate. In any solution in equilibrium with both barium sulfate and barium carbonate, the carbonate ion concentration must be 25 times the sulfate ion concentration. Therefore for the complete conversion of a formula weight of sulfate to carbonate there will be required a formula weight of sodium carbonate for the chemical reaction, and 25 formula weights of sodium carbonate to maintain the equilibrium ratio. This statement does not, of course, apply to a carbonate fusion of barium sulfate, for there the sodium carbonate is the solvent as well as the solute; but it does apply to aqueous solutions. This calculation has been made for 20°, but no smaller quantity of sodium carbonate could be used in a boiling solution safely, since the solution is cooled while filtering.

Suppose 2.33 grams (0.01 formula weight) of barium sulfate is shaken a long time with 100 c.c. of 1 formal soda solution, which contains 0.1 formula weight of sodium carbonate. Let

x be the mols of sodium carbonate remaining in solution at equilibrium, then $(0.1 - x)$ mols of sodium sulfate are in solution, and $(0.1 - x)/x = 0.04$, whence $x = 0.0962$ mols of sodium carbonate remaining. Then 0.0038 mols of sodium carbonate have reacted, forming 0.0038 mols of barium carbonate, and leaving 0.0062 mols of barium sulfate unchanged. It is clear that too little soda solution has been used. As stated above, the minimum quantity required is 26 times the mols of barium sulfate to be converted to carbonate, or 260 c.c. of formal sodium carbonate solution. Any quantity of this solution greater than 260 c.c. will therefore convert the sulfate completely to carbonate. Experiments of this kind may be used to determine the solubility product of one salt when that of another is known, since the equilibrium constant is the ratio of the two solubility products.

Silver reacts with ferric salts, forming ferrous salts and silver salts. The reaction is

$$Ag \text{ (solid)} + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2,$$

and the equilibrium expression is[1]

$$\frac{(Ag^+)(Fe^{++})}{(Fe^{+++})} = K = 0.128 \text{ at } 25°.$$

From this value of K it may be seen that unless the silver ion concentration is very small, complete reduction of ferric nitrate to ferrous nitrate will not take place. For example, suppose 0.2 formal ferric nitrate to be shaken with an excess of silver until equilibrium is reached. If x is the ferrous ion concentration, $(0.2 - x)$ is the ferric ion concentration, and x is the silver ion concentration, since the chemical equation shows that a silver ion is formed for each ferrous ion. Assuming substantially equal ionization of the salts, we have $\frac{x^2}{(0.2 - x)} = 0.128$, whence x is 0.132, the concentration of ferrous salt, and the ferric salt concentration is 0.068. This shows that only two-thirds of the ferric salt has been reduced. If some salt is added which precipitates silver ions as soon as formed, and which does not react with the iron salts, then in the presence of solid silver the ferric salt concentration must be very small compared to the ferrous salt concentration, or in other words, reduction is substantially complete. Addition of a thiocyanate serves this purpose,[1] and by this means iron may be reduced for titration, the thiocyanate furnishing at the same time an indicator for complete reduction. The excess thiocyanate is removed by adding silver nitrate solution just before the titration.

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[1] Noyes and Brann, *J. Am. Chem. Soc.*, **34**, 1,016 (1912).

Another reaction of this type is that between lead perchlorate and metallic tin,[2] according to the equation

$$\text{Sn (solid)} + Pb(ClO_4)_2 = Sn(ClO_4)_2 + \text{Pb (solid)}$$

for which $K = (Sn^{++})/(Pb^{++})$. The experimental results for 25° are as follows:

TABLE 98.—EQUILIBRIUM BETWEEN TIN AND LEAD PERCHLORATE

Molal concentration of solution at start of experiment		Equilibrium concentrations mols per liter		$K = \frac{(Sn^{++})}{(Pb^{++})}$
Tin perchlorate	Lead perchlorate	Sn^{++}	Pb^{++}	
0.094	.....	0.0704	0.0233	3.02
0.050	.....	0.0393	0.0123	3.19
0.050	.....	0.0413	0.0132	3.14
.....	0.096	0.0716	0.0237	3.04
.....	0.060	0.0457	0.0148	3.08
.....	0.050	0.0369	0.0119	3.11
0.038	0.019	0.0428	0.0145	2.96
0.051	0.037	0.0697	0.0239	2.92
0.066	0.027	0.0692	0.0235	2.95
0.086	0.024	0.0821	0.0275	2.98

In some cases the starting solution contained lead perchlorate alone, or tin perchlorate alone, in other cases both perchlorates were present in solution; excess of both solid metals was always used. These solutions were shaken at 25° with solid tin and solid lead until they had reached equilibrium. As shown by the value of K in the last column of the table, the ratio of tin salt to lead salt at equilibrium is about 3.0, whether the reaction proceeded in one direction or the other, and regardless of the relative quantities of tin perchlorate and lead perchlorate in solution at the start of an experiment. This is a strong confirmation of the principles involved in equilibrium formulations.

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[1] Edgar and Kemp, *J. Am. Chem. Soc.*, **40**, 777 (1918).

[2] Noyes and Toabe, *J. Am. Chem. Soc.*, **39**, 1,537 (1917).

It is necessary that the solid phases present be those written in the equation however. The equilibrium ratio does not apply unless both solids are present, and quite another constant may be obtained if some solid forms which does not appear in the chemical equation.

Thus, we should formulate the equilibrium expression for the reaction

$$CaSO_4 \text{ (solid)} + Na_2CO_3 = CaCO_3 \text{ (solid)} + Na_2SO_4$$

in the usual way,

$$\frac{(SO_4^{--})}{(CO_3^{--})} = K = \frac{S_1^2}{S_2^2} = \frac{2.3 \times 10^{-4}}{3 \times 10^{-9}} = 7 \times 10^4$$

from which the sulfate ion concentration at equilibrium is seventy thousand times the carbonate ion concentration. Direct experiment[1] gives quite another value however, owing to the fact that at equilibrium the solid phases present are not calcium carbonate and calcium sulfate. A solid, gaylussite, of the composition $CaCO_3.Na_2CO_3.5H_2O$, forms, and therefore the equilibrium ratio does not conform to that formulated above on an incorrect assumption as to the nature of the solids present. According to experiment, the ratio of sulfate to carbonate is 19 in these solutions. But when the solids present are those shown by the chemical equation, substantial agreement is obtained between calculated concentration ratios and those based on experiments.

Phase Diagrams[2] (Pressure-temperature Diagrams).—Many substances form, in addition to a vapor and a liquid, two or more solid phases. These solids are of different crystalline form, solubility, and physical properties, but they have the same chemical composition. "Grey" tin and "white" tin, rhombic and monoclinic sulfur, red phosphorous and white phosphorus, are familiar from elementary chemical study; the several modifications of ice produced under high pressure are perhaps less well known. Diagrams showing the temperature and pressure corresponding to the existence of various single phases, pairs of phases, etc., are commonly called phase diagrams. Any single phase in a system composed of only one chemical substance may exist throughout a certain temperature range and under a variety of pressures; two phases co-exist at a certain definite pressure for each temperature, and cannot exist at any other pressure at this temperature; when three phases are present at equilibrium in a system of one chemical substance, neither the temperature or pressure can be varied. For example, liquid water may exist under any pressure greater than its vapor pressure, and any temperature above the freezing point and below the boiling point corresponding to the pressure imposed, but liquid water and water vapor exist at any chosen temperature only under the vapor pressure. If at 100° the external pressure is maintained at less than 1 atmosphere, no liquid water condenses; if the pressure is made greater than 1 atmosphere, all of the vapor condenses. Only when the pressure is exactly 1 atmosphere can liquid water and water vapor exist at 100°. Under these conditions however, the two phases can exist at equilibrium in any relative quantities whatever; a drop of liquid in contact with a large volume of vapor, or a single bubble of vapor in equilibrium with a large quantity of liquid.

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[1] Herz, *Z. anorg. Chem.*, **71**, 206 (1911).

[2] Many other phase diagrams will be found on pages 611–697 of *Landolt-Börnstein's Tables;* and in Hall and Williams' "Microscopic Analysis."

Only at the freezing point and under the vapor pressure of ice can all three phases exist. Thus the presence of three phases in a system of one component[1] fixes both the temperature and the pressure. This is therefore an invariant system. A two-phase system of one component may exist at one particular pressure for each temperature; or at one particular temperature for each chosen pressure. Since one condition (pressure or temperature) of such a system may be arbitrarily fixed, it is a univariant system. A general relation between the number of phases, the number of components and the variance of a system at equilibrium will be taken up in the next section.

A simple diagram of this character, describing the phases of water, is shown in Fig. 37. The line *BDE* is a vapor pressure line, *i.e.*, a line showing the pressure at which liquid and vapor may exist at equilibrium for every temperature. At 60° the vapor pressure is 0.196 atmosphere; accordingly if water at 60° is acted upon by a greater pressure, all of it remains as liquid, if the pressure is reduced below 0.196, liquid vaporizes until the equilibrium pressure is reached or until all of the liquid is exhausted. At a lower pressure than 0.196 atmosphere the system, water at 60°, consists of vapor only. Hence the line *BDE* is a two-phase line, defining the pressure at which two phases co-exist for each temperature on the diagram. The temperature at which ice and liquid water exist in equilibrium under a pressure of 1 atmosphere is defined as 0° on the Centigrade scale; but since the vapor pressure of ice at 0° is only 0.006 atmosphere, this is not the temperature at which all three phases exist. As calculated on page 94 the melting point of ice is lowered 0.0076° for each atmosphere increase of pressure; hence at 0.006 atmosphere the equilibrium temperature is essentially +0.0076°, and this is the three-phase temperature or

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[1] The components of a system are the chemical substances required to make each of its phases in whatever quantity they may be present, Thus the substance water is capable of forming all of the phases of this system, but if the system under consideration is a solution, water and the salt are its components,

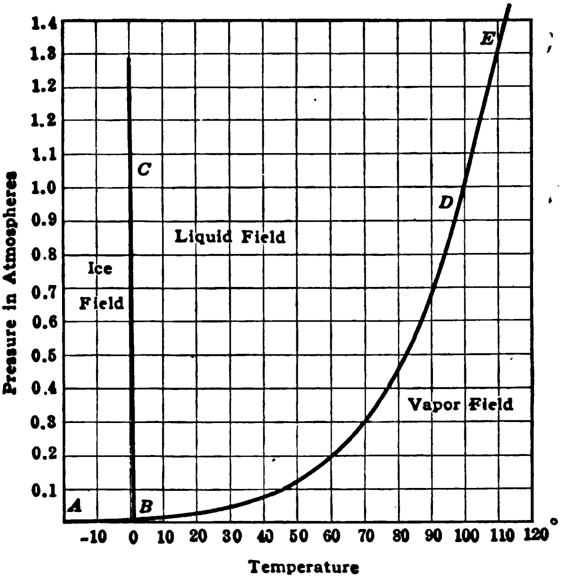

Fig. 37.—Phase diagram for water.

triple point. The pressure at the triple point is 0.006 atmosphere, which is the vapor pressure of both ice and water at 0.0076°, since they are in equilibrium with each other at this temperature. The slight effect of pressure upon the melting point of ice (*i.e.*, the equilibrium between solid and liquid) is shown by the slope of the line *BC* of Fig. 37 to the left.

A consideration of the phases of urethane[1] will further illustrate phase diagrams. It forms a vapor, a liquid, and three different solid phases, which we may designate by I, II, and III. On account of the high pressures involved in the formation of III, the vapor field does not show in the diagram. As urethane boils at 180°, the vapor field would occupy only a very small area at the bottom of the diagram, corresponding to vapor pressures of less than 1 atmosphere for the temperature range shown. The position of this vapor field is indicated in Fig. 38, showing the pressures and temperatures at which each of the other phases exists.

Between 52 and 70° equilibrium between liquid and solid I is shown by the line *ab*. It will be noted that this line slopes in the opposite direction to the liquid-solid line for water, indicating that an increase of pressure raises the melting point. As increase of pressure always results in the formation of a more dense substance; solid I is more dense than liquid, and will sink in it. At 70° and 2,200 atmospheres (*b*) there is a change in the character of the solid phase, and during transition from I to II there are three phases present. This is therefore an invariant point, and neither temperature or pressure can change until some phase disappears. Which one will be exhausted first depends upon the conditions of experiment. If heat is added to the system, and such a pressure is maintained that liquid is always present, phase I disappears, and the equilibrium between II and liquid is shown by the line *bc*. The point *c* corresponds to another triple point involving the liquid phase; point *d* is the triple point of all three solids. From experimental determinations of the pressure and temperature of these three triple points, together with the transition pressure of I to III at 0°, the melting point of I at 1 atmosphere, and the melting point of III at 8,000 atmospheres, the diagram of Fig. 38 has been constructed. Point *a* is 52° and 1 atmosphere, *b* is 70° and 2,200 atmospheres, *c* is 80° and 4,100 atmospheres, *d* is 25° and 3,400 atmospheres, *e* is 0° and 3,000 atmospheres, *f* is 120° and 8,000 atmospheres.

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[1] Bridgman, *Proc. Amer. Acad.*, **52**, 57 (1916); *Proc. Nat. Acad.*, **1**, 513 (1915).

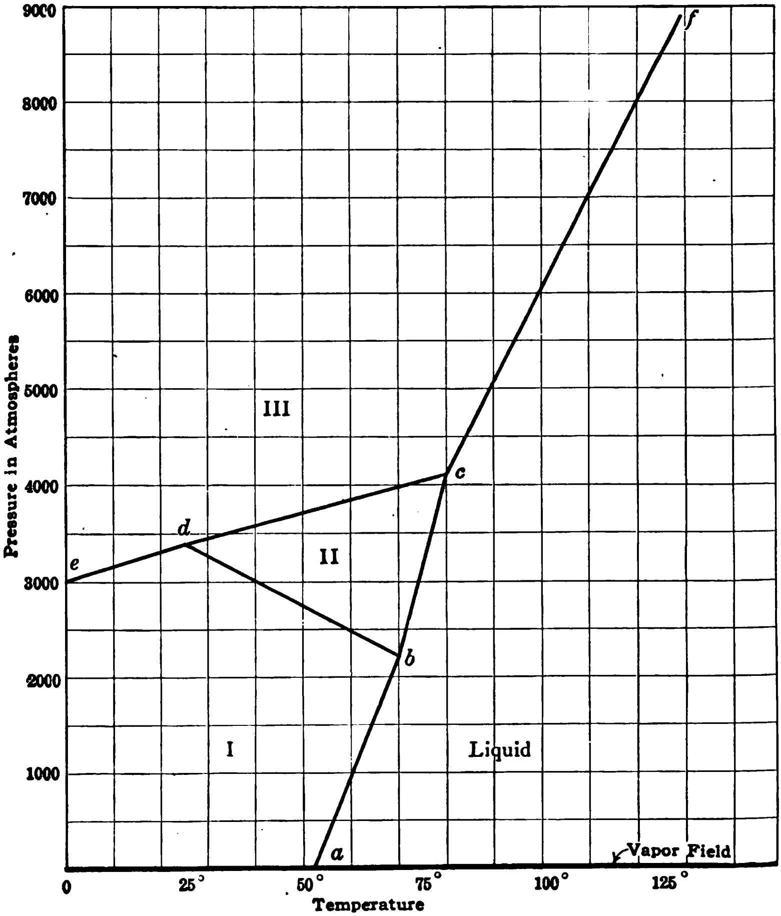

FIG. 38.—Phase diagram for urethane.

Suppose a quantity of urethane to be kept at 60° while (through the steady motion of a piston in a cylinder containing it) its volume is slowly decreased. As the melting point is 52°, the system consists of a liquid at the start; a one-phase, one-component system may exist under various temperatures and pressures, but we have fixed arbitrarily upon a temperature of 60°. The system remains liquid as the volume of it decreases until a pressure of about 900 atmospheres is reached, that is, a point on the line *ab*. Here phase I appears, and until all of the liquid is changed to it we have a two-phase system at a fixed temperature. Hence the pressure will remain constant while the volume decreases to that of the solid alone. As heat is evolved during the solidification, it must be removed from the system in order to keep it at 60°. Finally, all of the liquid changes to solid I, and a further movement by the piston causes an increase of pressure in the system. When a pressure of 2,100 atmospheres is reached (line *bd*), I changes to II at a constant temperature and pressure, with a further decrease in volume. Then II is compressed until the pressure reaches about 3,800 atmospheres (line *dc*), where it changes to III. Further decrease in volume does not cause the appearance of any new phases.

Let us consider another case, a steady heating under constant pressure. When this takes place under a pressure of 1 atmosphere, melting occurs at 52°, vaporization at 180°, and no other phases are formed. Suppose we start with urethane at 0° and a pressure of 3,200 atmospheres. Reference to Fig. 38 will show that the system is solid III under these conditions. If the pressure is maintained at 3,200 atmospheres by suitable motion of the piston confining it, and heat is added slowly, no phase change occurs until about 10°. Here heat will be absorbed while solid III is changed at a constant temperature to solid I. It will be noted that addition of heat at this point (on the line *ed*) does not cause a rise of temperature but causes the transition of III to I. As is always the case, a phase stable at high temperatures is formed from one stable at a lower temperature with the absorption of heat. During transition both phases are present at a fixed pressure, hence the temperature cannot change until one phase is exhausted. When all of III has changed to I, further addition of heat raises the temperature steadily until about 30°, where I changes to II with the absorption of heat, in the manner just explained. Phase II is stable at 3,200 atmospheres from 30° to 75°, where it melts with the absorption of heat, as in the case of all melting solids.

Heat Effects of Phase Changes.—The Clausius-Clapeyron equation can be used to calculate the heat absorbed during any of these phase changes, when the change of the transition point with pressure is known, or when it can be read off from a phase diagram. If Δv is the increase in volume attending transition of a gram of substance from one phase to another at the temperature T, and if dp/dT is the change in transition pressure in atmospheres per degree, the heat quantity L will be in cubic centimeter-atmospheres absorbed per gram. These units may be converted to calories by dividing by 41.24.

Gibbs' Phase Rule.—Before giving the general statement of phase equilibrium known as Gibbs' "phase rule," it will be necessary to define again the terms in it. The *phases* of a system are its homogeneous parts which are separated from one another by definite physical boundaries; thus there may be in a system only one gaseous phase, for all gases mix with one another in all proportions; a solution is one phase, but two liquid layers (such as water and benzene) constitute two separate phases, and each crystalline substance present is a separate phase. The *components* of a system are the chemical substances necessary to form all of its phases in any relative quantities. For example, one system composed of lime, calcium carbonate, and carbon dioxide may be made from a single substance, calcium carbonate. But it is possible for these three phases to exist together when the amount of lime is not chemically equivalent to the carbon dioxide present. Since all three substances may be formed in any desired quantity from lime and carbon dioxide, these two substances may be called the components of the system. It would serve equally well to designate the components as lime and calcium carbonate, for by adding or removing these two substances any desired quantity of each phase could be brought into a system. This is then a two-component system. The *degree of freedom* of a system, also called the *variance* of it, is the number of external conditions which may be arbitrarily fixed; the only conditions commonly considered are the temperature and pressure of the system as a whole.

Denoting by P the number of phases in a system, by C the number of components, and by V the variance, Gibbs' rule is

$$P + V = C + 2.$$

This is a *qualitative* law limiting the number of phases which may exist together at equilibrium in a system. It tells nothing whatever as to *what* phases exist, but only the number which exist under specified conditions. Let us consider the system CaO, CO_2, $CaCO_3$, which is a two-component system, since the third phase may be made from the first two. When all three phases exist, application of Gibbs' equation shows that $V = 1$. This means that all three phases may exist in equilibrium at different temperatures provided the pressure is not specified, or at different pressures provided the temperature is not specified. Since $V = 1$, either pressure or temperature may be specified, but not both. And this freedom is only within certain limits, imposed by the chemical properties of the system. Thus we may not specify that a system composed of only these substances shall exist at 4,000°C., for at that temperature carbon dioxide dissociates into carbon monoxide and oxygen to a certain extent, and there are other chemical substances present which were not present in appreciable quantity at lower temperatures. But suppose we say that all three phases of this system shall exist at 900°, we must adjust the pressure to the dissociation pressure of limestone at 900° (760 mm.); if we have this three-phase system at 800°, the pressure must be the dissociation pressure corresponding to this temperature (180 mm.). Of course we might have specified the pressure of 760 mm., and sought the temperature at which this dissociation pressure exists.

Suppose we specify that this system shall be brought to 600° and 1 atmosphere, we have taken $V = 2$; application of the equation to determine the number of phases existing under these conditions shows that $P = 2$. Hence some two phases of this system can exist together at this temperature and pressure, but the phase rule says nothing as to what the phases are. They may be lime and calcium carbonate, carbon dioxide and calcium carbonate, but not lime and carbon dioxide, for the specified pressure is greater than the dissociation pressure of calcium carbonate at this temperature. It should be further noted that the phase rule gives only the maximum number of phases, and that it does not state that one phase may not exist alone at a specified temperature; only that there shall not be more than two phases.

Temperature-Composition Diagrams.—Most experimental work is carried out under a pressure of 1 atmosphere. It is convenient and instructive to show by diagrams the conditions of equilibrium in two-component systems of varying composition at different temperatures, when the pressure is maintained constant. While these diagrams are sometimes called phase-rule diagrams, they are not properly mere applications of the phase rule. This rule is qualitative only; the diagrams show quantitatively the conditions of equilibrium in a system. We shall consider only two-component systems. In these diagrams the abscissæ show the composition of the *system as a whole*, ordinates show temperature variations. Certain vertical lines in the diagrams therefore correspond to the composition of some particular phase of the system. Solubility curves are familiar examples of such diagrams; as are also curves showing the freezing point of a solution as a function of the composition. Such diagrams are of prime importance in the study of alloys, which are usually solutions of metals in metals, and which often form metallic compounds. Let us consider first a simple freezing point-composition diagram for a two component system.

System: Lithium Chloride and Potassium Chloride.—Fused potassium chloride dissolves lithium chloride, which thereby lowers the freezing point of the solution, *i.e.*, the temperature at which the liquid is in equilibrium with solid potassium chloride. The data are as follows:

Mol per cent of LiCl....	0	34.3	39.5	42.6	55.8	58.5
Freezing point..........	773°	600°	552°	527°	385°	361°

But potassium chloride is soluble in fused lithium chloride also, and it lowers the freezing point of lithum chloride. The following are the experimental results:

Mol per cent lithium chloride..............	100	64.4	59.4	58.5
Freezing point...........................	601°	412°	372°	361°

When the mol per cent of lithium chloride in solution is 58.5, the liquid is in equilibrium with both solid KCl and solid LiCl at 361°, this is called the eutectic point. Upon plotting these figures in a diagram in which the mol fraction of lithium chloride *in the system* is shown as abscissæ, Fig. 39 results.[1] The field above *abcde* is the liquid field; systems of any composition consist of liquid solution of one salt in the other at all points above this line. Let us study the behavior of a solution in which the mol fraction of lithium chloride is 0.35, when it is cooled from 700° to 300°; the path of which process is indicated by the dot-and-dash line on the figure. At 700° the system under a pressure of 1 atmosphere consists of solution alone, and it remains liquid until about 600° (point *b* on the diagram).

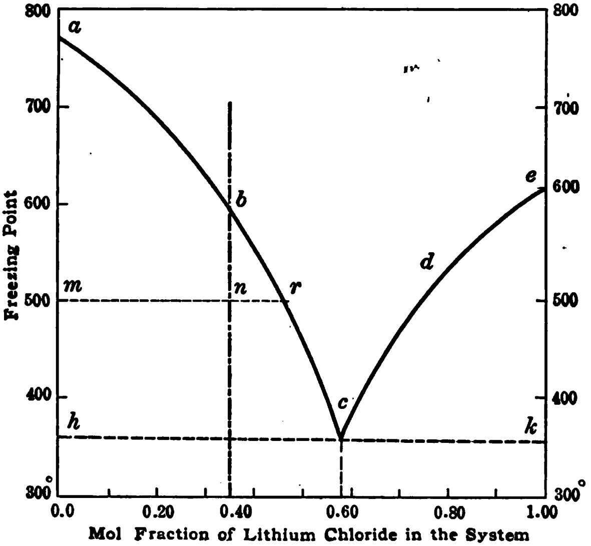

FIG. 39.—Phase diagram for lithium chloride in potassium chloride.

At this temperature solid potassium chloride begins to separate from the melt. The composition *of the system* remains constant, but a new phase appears whose composition is shown by the left hand margin (*i.e.*, pure potassium chloride); and owing to the separation of pure potassium chloride from the melt, the mol fraction of lithium chloride in the melt increases; at 500° considerable solid potassium chloride will have separated out, and the mol fraction of the melt is about 0.45 in lithium chloride.

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[1] Richards and Meldrum, *J. Am. Chem. Soc.*, **39**, 1,816 (1917). Similar diagrams are obtained for systems composed of AgCl and KCl, $BaCl_2$ and $CaCl_2$, AgCl and RbCl.

If heat has been withdrawn from the system at a uniform rate of so many calories per minute, the fall of temperature will take place more slowly after reaching *b*, owing to the heat evolved when potassium chloride solidifies. As the cooling proceeds, more solid separates, and the composition of the melt is shown for each temperature by the line *bc*, until at 361° the liquid is saturated with both potassium chloride and lithium chloride; both salts separate at this point, and the temperature remains constant until all liquid disappears. As this is a three-phase point at a specified pressure, no further variance is possible in the light of the phase rule.

Let us return to a consideration of the system at 500°, which is at the point *n* in the field *ahc*. The system contains 0.35 mol of lithium chloride to 0.65 of potassium chloride, but one phase of the system is pure potassium chloride, hence the other phase must be poorer than the system as a whole in this component. There is another fact to be derived from the dimensions of the diagram; namely that the relative quantities of solid potassium chloride and of solution at 500° are to each other as the lengths *nr* and *nm*. At *b* the length *nr* is zero, which means that no solid potassium chloride has separated yet; at 400° the length of *nr* is longer in proportion to that of *mn*, corresponding to a further separation of potassium chloride as the temperature is lowered.

We may also designate the phases existing in a system whose composition *as a whole* is shown by the abscissæ at any temperature. In the field above *abcde* such a system is liquid only; in the field *ahc* it consists of solid potassium chloride and solution of the composition shown along *abc*; in *cke* it consists of solid lithium chloride and solution of the composition *cde*; below the line *hck*, of a mixture of the two solid salts. This diagram is typical of all two-component systems if the substances mix in all proportions in the liquid state, and provided they do not form a compound; it is the simplest type of such diagrams.

Cooling Curves.—If the temperature of a system undergoing cooling at a uniform rate is measured every minute, and a diagram showing these temperatures against time as abscissæ is drawn, a curve is obtained in which abrupt changes in slope indicate the processes occurring during cooling. In the cooling just discussed, from 700° to 600° there is no process occurring in the system which evolves heat except the cooling process. At 600° solid potassium chloride begins to separate, giving rise to more heat, and hence the rate at which the temperature falls is slower, though heat is being withdrawn from the system at a constant rate. There will therefore be a break in the slope of the curve at this point (1 in Fig. 40). At 361°, where both solids are separating, since this is a three phase point in a two component system under a specified pressure, the temperature remains constant (2, 3) even though heat is being taken from the system; the heat evolved is the latent heat of solidification of the component salts. Such a curve is shown in Fig. 40, line *A*.

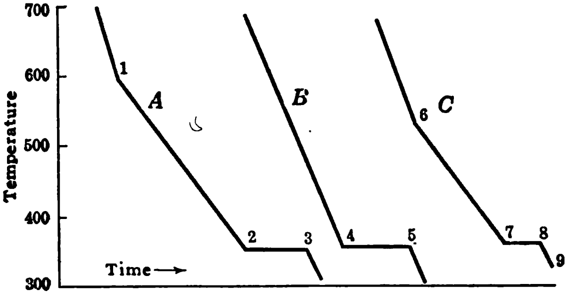


Fig. 40.—Cooling curves for the system shown in Fig. 39.

Line *B* of Fig. 40 is a cooling curve for a solution of composition 0.585, which deposits both solids at 361°; line *C* shows a cooling curve for a solution containing 80 mol per cent of lithium chloride. At the point 6 (520°) solid lithium chloride begins to separate, and the composition of the melt changes along the line *edc* of Fig. 39 as the temperature falls; at point 7 (361°) both solids separate, as in cooling the other solutions. For pure lithium chloride a cooling curve would have the same form as *B*, with the horizontal portion at 601°, the melting point of the pure salt.

Thermal Analysis.—In any given piece of apparatus the time interval during which eutectic is forming is proportional to the weight of eutectic; that is, the eutectic weights are proportional to the lengths of the horizontal portions of such curves as those of Fig. 40. If therefore the lengths of the horizontals for fixed weights of various mixtures are plotted vertically against the composition of the system as a whole, a triangle is obtained which has its apex over the eutectic composition. This must be so, since a solution of the same composition as the eutectic solidifies entirely at one temperature. From this plot it is possible to analyze an unknown mixture of the two components by determining the length of time required to solidify all of its eutectic in the standard apparatus. Knowing then the weight of system taken, we may calculate from the weight of eutectic the percentage of each component. It is necessary to determine in some other way whether the given sample lies on the right or left hand side of the eutectic; but this is usually known, or may be estimated from specific gravity or some other easily determined property.

Two-Component System in which a Compound Forms.—If the two components of a system mix in all proportions in the liquid state, but form a solid compound, a diagram of somewhat different character shows the phase equilibrium. Each component dissolves in the compound to lower its freezing point; and the compound dissolves in each pure component to lower its freezing point. Let us build up such a diagram from the corresponding cooling curves for the system magnesium and tin. It will be seen from Table 99 that the compound formed contains 71 per cent of tin by weight, or $\frac{71}{119} = 0.59$ atomic weights of tin to $\frac{29}{24.3} = 1.18$ of magnesium; that is $SnMg_2$, and that it melts at 785°. Further, the eutectic formed of pure tin and compound solidifies at 565° and that composed of compound and magnesium solidifies at 210°. Our diagram will consist of two portions, each similar to Fig. 39. The composition of the second eutectic is shown by the 97 per cent solution solidifying all at one temperature; that of the other eutectic is not given, but may be obtained as shown below.

TABLE 99.—SYSTEM: MAGNESIUM AND TIN

Weight per cent of tin in the system	0	20	30	50	60	71	80	90	97	100
First break in cooling curve	650°	610°	585°	675°	750°	785°	700°	400°	210°	232°
Horizontal portion of cooling curve	650°	565°	565°	565°	565°	785°	210°	210°	210°	232°

Inserting the known points on a diagram and connecting with lines, we obtain the diagram of Fig. 41, and by extending the freezing curves smoothly, the first eutectic is seen to contain about 35 per cent of tin. The left hand 71 per cent of this diagram corresponds to the two-component system magnesium-Mg_2Sn; the right hand 29 per cent to a system Mg_2Sn-tin; but it is convenient to cover the whole range on a single sketch. Each portion of this diagram may be treated exactly as was Fig. 39. The relative weights (since the plot shows percentage by weight) of compound and liquid melt in a system consisting of 50 per cent by weight of tin at 600° are to each other as the lengths *nr* and *mn* on this diagram. When the cooling of a system containing 85 per cent of tin is carried out as indicated on Fig. 41 by the dot-and-dash line, compound separates from the melt at 590° and the melt changes composition during cooling as shown by the line *cd* until 210° is reached, where both compound and pure tin separate at a constant temperature until all of the liquid phase is exhausted.

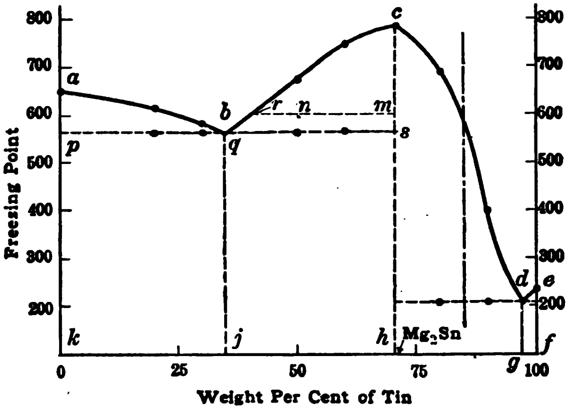


FIG. 41.—Phase diagram for the system magnesium and tin.

The Eutectic Mixture.—This is often referred to as "the eutectic," but it should be clearly understood that it is a mixture of two separate phases There is no such thing as the "eutectic phase." When an alloy is cooled, the component which first separates appears in larger crystals than those forming at the eutectic temperature. Then both solid phases separate at once at the eutectic temperature, in an intimate mixture which is of finer grains than the crystals of single component already separated, but this will be seen under a microscope to consist of separate crystals of each substance. The maximum point at *c* in Fig. 41 indicates that a compound has been formed, but the minimum points *b* and *d* do not correspond to compounds. A system of the composition shown by point *n* in this diagram consists of solution of composition *r* and solid of composition *m*, which is the compound Mg_2Sn; these two phases are present in the relative weights, solution : compound = *nm* : *nr*, just as in the simple diagram of Fig. 39.

Systems which form a compound have in general this type of diagram when the solid phases are those indicated, but before applying these considerations to a given system, it is first necessary to ascertain that the solid phases are those which are to be written on the diagram. As in the case of reactions involving solutions and solids, the equilibrium conditions cannot be represented quantitatively on a diagram unless the exact nature of the solid phases is known.

Solid Solutions.—So far we have considered in connection with freezing points only those cases in which a pure substance separates on cooling. In the case of alloys, and less frequently in other melts, the solid crystal which deposits is a perfectly homogeneous mixture of the two components. It is not a fine crystalline meal of pure crystals of each component as in the eutectic, but a single crystal containing in its lattice two kinds of metal atoms. These are sometimes called mixed crystals, more often solid solutions; and as is the case in liquid solutions, they are of indefinite proportions. Some substances form solid solutions in all proportions, just as some liquids mix in all proportions; others have only limited solubility.

The case of total miscibility is parallel to the partial condensation of a vapor from a liquid mixture, which was considered under fractional distillation. A simple example is the alloy of copper and nickel, for which the "freezing points" are as follows:

Per cent copper	0	25	50	75	100
Apparent "freezing point"	1,450°	1,400°	1,310°	1,210°	1,080°

These temperatures might better be called the solidification temperatures, since a freezing point is the temperature at which a solution is in equilibrium with pure solid solvent, and the crystal which separates in this case is a solid solution.

A liquid solution containing 25 per cent of copper deposits upon cooling a first crystal containing 10 per cent of copper; the 50 per cent solution deposits a crystal containing 30 per cent, and the 75 per cent solution gives a crystal containing 55 per cent of copper. In each case, these figures refer only to the first small portion of solid deposited; as the temperature falls the composition of the liquid changes, that of the solid also changes, as in the fractional condensation of vapors. The average composition of the whole solid alloy is of course the same as that of the liquid melt, but the first portion of solid separating is poorer in copper than the original liquid, the last drop of liquid to solidify is richer in copper than the original melt. The temperature at which deposition of solid begins is shown in Fig. 42 by the solid line; the composition of the solid solution first deposited from each solution is shown by the dotted line. The phase fields may be written upon this diagram, as in other temperature-composition diagrams. Below the dotted line all of the alloys of nickel and copper are solids, above the solid line all of them are liquids. In the field between these lines, two phases exist. For example, at 1,260° a system composed of 60 per cent copper and 40 per cent nickel consists, at equilibrium, of a solid solution containing 50 per cent copper (point *a*) and a liquid solution containing 70 per cent copper (point *b*). If such a system were cooled from

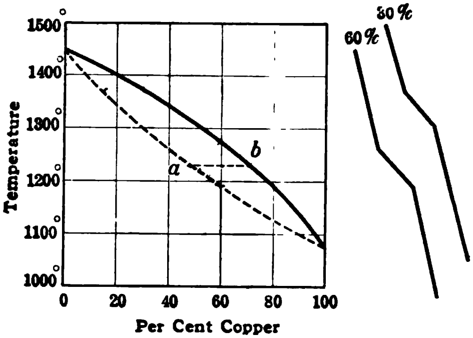
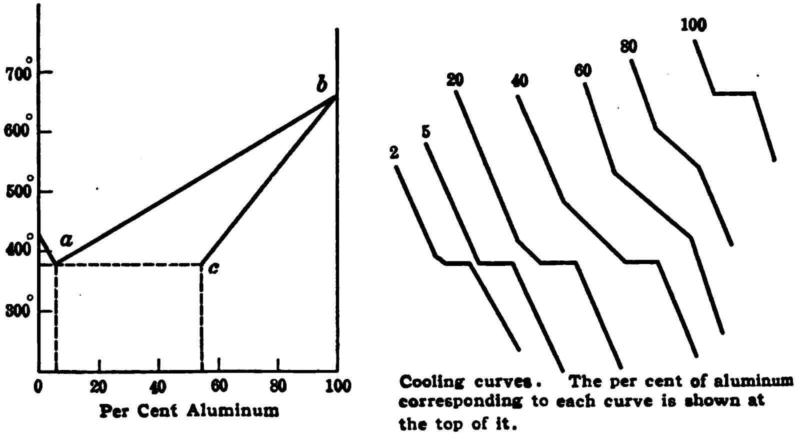


FIG. 42.—Phase diagram for the system copper and nickel.

1,500° to 1,000°, the first crystal deposited would contain about 35 per cent of copper (and would appear at about 1,275°), the last drop of liquid to solidify would contain about 80 per cent of copper, and solidification would be complete at 1,190°.

At the right of Fig. 42 are shown two typical cooling curves for such a system. The portion between the two breaks corresponds to the range in which solid is depositing. As each liquid deposits a solid of different composition, there is no horizontal portion in such curves. A solid solution is one phase, and a horizontal portion in a cooling curve for a two-component system demands two solid phases and a liquid phase.

Solid Solutions. Incomplete Miscibility.—Alloys of aluminum and zinc do not form solid solutions over the whole range of composition from pure zinc to pure aluminum, and the two metals do not form a compound. Solutions containing less than 5 per cent of aluminum deposit upon cooling pure zinc crystals until the eutectic is reached. The two phases forming the eutectic are pure zinc and a solid solution containing 55 per cent aluminum. This is the saturated solid solution; and solutions containing more than 55 per cent of aluminum are not saturated with zinc. Thus a melt containing 60 per cent of aluminum begins at 540° to deposit a solid solution containing 80 per cent of aluminum; as the temperature continues to fall, the composi-



Cooling curves. The per cent of aluminum corresponding to each curve is shown at the top of it.

FIG. 43.—Phase diagram for the system aluminum and zinc.

tion of liquid melt changes along the line *ab* of Fig. 43, that of the solid deposited from it changes according to the line *cb*. A 40 per cent melt deposits at 480° a solid solution of about 70 per cent aluminum, and as the temperature is lowered, the melt changes its composition along *ab* until the eutectic temperature of 380°, where zinc and the saturated solid solution are deposited. The behavior of these alloys will be made clearer from a careful study of the cooling curves of Fig. 43. The student should determine from the phase diagram what phases are in equilibrium along each portion of each curve given, and tabulate these results.

Partially Miscible Liquids.—Aniline and hexane are only partially soluble in one another[1] at room temperatures, but each solubility increases as the temperature is raised and at about 60° the miscibility becomes complete. The temperature 60° is called the critical solubility temperature. If a solution containing 50 per cent of each liquid is cooled, it separates into two layers just below 60°, one of which follows down each branch of the curve of Fig. 44. At 20° one layer consists of about 8 per cent hexane (this is a saturated solution of hexane in aniline) and the other consists of 93 per cent hexane (saturated solution of aniline in hexane). The vapor pressures of the components from each of the phases are greater than those computed from Raoult's law, indicating that the two substances have little attraction for one another, as is also shown by the slight solubility.

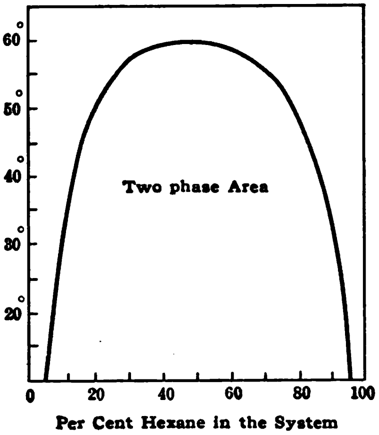


FIG. 44.—Solubility of aniline in hexane.

Within the area under the curved line, a system of aniline and hexane having the composition shown on the bottom of Fig. 44 consists of two mutually saturated solutions; as the temperature is raised, each solution takes on some of the "solvent" in the other, that is, the mol fraction of "solute" in each layer increases as shown, until at the critical solubility temperature the liquids mix with each other in all proportions. The temperature of this critical solubility for several other liquid systems which form two layers at room temperature is shown in the table below. In every case the maximum point in the solubility curve occurs in the diagram over the point corresponding to about 50 per cent of each component. In these systems the average composition of the two layers is a straight-line function of the temperature,[1] a fact corresponding to the law of linear average densities for liquid-vapor systems. (Law of Cailletet and Mathias, page 79). This rule is of use in determining the exact composition corresponding to the critical solubility temperature. These critical solubility temperatures are often far above the boiling points of the components, so that complete solubility is not attained without the application of considerable pressures.

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[1] Keyes and Hildebrand, *J. Am. Chem. Soc.*, **39**, 2,126 (1917).

TABLE 100.—CRITICAL SOLUBILITY TEMPERATURE

System	Critical solubility temperature
Water and nitrobenzene	245
Water and *o*-nitrotoluene	262
Phenol and isopentane	66
Aniline and isopentane	79
Phenol and hexane	43
Phenol and octane	50

Solubility of the Hydrates of Zinc Nitrate.[2]—The diagram of Fig. 45 represents equilibrium between the phases of a system composed of zinc nitrate and water. The possible solid phases within the temperature and composition range of this diagram are ice, solid $Zn(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$ and $Zn(NO_3)_2$-$9H_2O$; the liquid phase is a solution of zinc nitrate in water, and there is no vapor phase present, since the data refer to a pressure of 1 atmosphere, and none of the constituents has a vapor pressure as large as 1 atmosphere within the temperature range there considered. The composition of the *system as a whole* is shown on the bottom of the diagram.

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[1] Campetti and Grosso, *Nuovo cimento*, **6**, 379 (1913).

[2] Mylius and Funk, *Wiss. Abh. Phys.-Tech. Reichsanstalt*, **3**, 438 (1900).

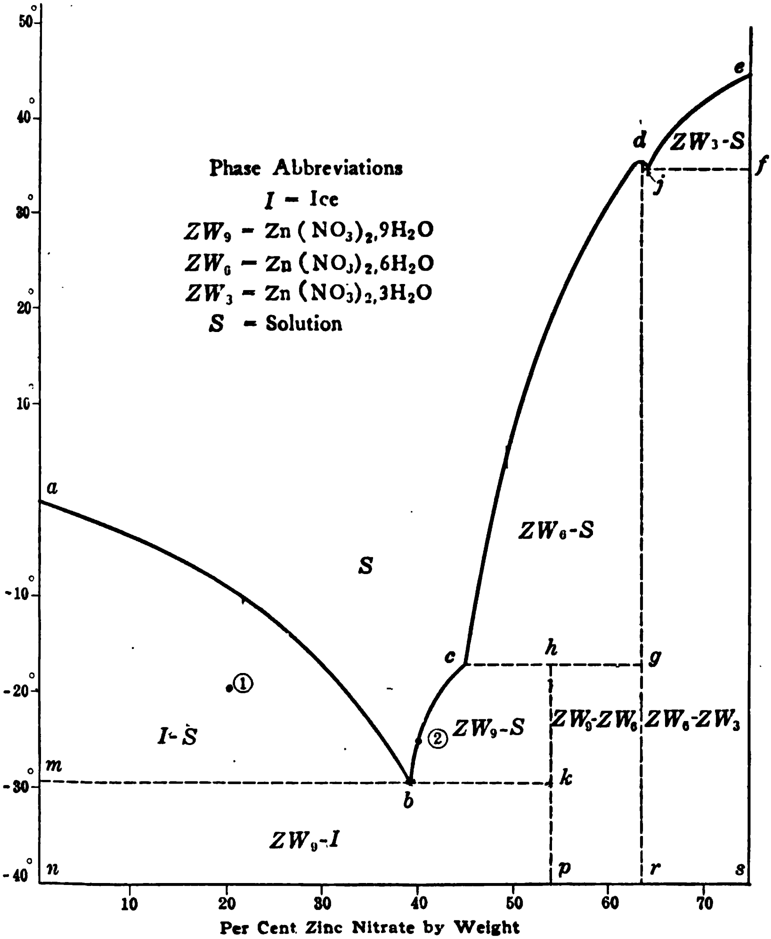

FIG. 45.—Phase diagram for zinc nitrate and water.

Curve *ab* of the figure represents the freezing-point curve for zinc nitrate solutions whose compositions in per cent by weight of anhydrous zinc nitrate are shown on the bottom axis. The freezing point of each solution may be read off at the left hand margin. A solution containing 20 per cent zinc nitrate by weight freezes at −9°; further cooling of this solution results in depositing more ice, with the formation of a solution containing a larger percentage of zinc nitrate. At −20° the system whose composition as a whole is 20 per cent zinc nitrate (shown at point 1) consists of ice and a solution containing 33 per cent of zinc nitrate. Further cooling of this 20 per cent system causes the solution to increase its concentration along the line *ab*, with the separation of more ice, until at −29° the eutectic temperature is reached, and solid $Zn(NO_3)_2.9H_2O$ appears. This is then a three-phase system under an arbitrary pressure of 1 atmosphere, and since it is a two-component system, three phases make the system invariant. The phase rule is

$$P + V = C + 2,$$

hence with three phases, the variance, or degree of freedom of the system, is unity, and the arbitrary condition of pressure has already been imposed. Further withdrawal of heat causes the solution to deposit ice and solid $Zn(NO_3)_2.9H_2O$ at a constant temperature until all of the solution is exhausted, after which cooling produces no new phases. When any solution of zinc nitrate containing less than 39 per cent of the salt by weight is cooled, it behaves in this manner, depositing ice at the temperature shown by the line *ab*, and increasing the concentration of the solution until −29° is reached, where the whole system solidifies.

Curve *bc* shows the solubility of $Zn(NO_3)_2.9H_2O$ in water as a function of the temperature. For the sake of brevity, we shall write this hydrate ZW_9 to indicate nine molecules of water to one of zinc nitrate. At −25° if the system as a whole has the composition 40 per cent Z (point 2), it consists of solution alone. If the temperature is reduced to −28°, ZW_9 separates out, and the system consists of two phases. (It should be made clear that the figures at the bottom of the diagram refer to the composition of the system *as a whole*, and that this is not the composition of any phase of the system unless the whole system consists of a single phase, as it does above or on the line *abcde*, for example.) When this solution is cooled to −29°, ice separates, and the system then consists of three phases, ice, ZW_9, and solution. Since one arbitrary condition has been imposed upon the system, a pressure of 1 atmosphere, this is in the light of the phase rule a non-variant system, and the temperature remains constant while heat is withdrawn from the surroundings until all of the solution is changed to ice and solid ZW_9. The system is then in the field *mkpn*, and further cooling forms no new phases. Any solution containing between 39 and 45 per cent Z which is gradually cooled will begin to deposit ZW_9 when the line *bc* is reached, and will continue to deposit this phase until −29° is reached. This is the eutectic temperature, and both ice and ZW_9 are formed until the solution is exhausted. At any point within the field *bkhc*, the system consists of solution in equilibrium with solid ZW_9. Suppose a system of 50 per cent Z were heated slowly from −25°, it would consist of solid ZW_9 and its saturated solution until −17° is reached. This is the transition temperature of ZW_9 to ZW_6, and hence at this temperature a new phase appears. The system is then an invariant one; heat is absorbed at constant temperature and used to change ZW_9 into ZW_6 until all of the former is exhausted, and the system again consists of only two phases. Further heating causes the solution to increase its concentration as shown by the line *cd* until at +5° all of the solid ZW_6 is dissolved, and a single-phase system results.

From the molecular weights of zinc nitrate and of water it may be computed that ZW_9 contains 53.9 per cent of Z by weight. Suppose pure ZW_9 to be heated from −40° (point *p*) to +40° by a slow, uniform addition of heat to the system. It remains one phase until −17° is reached (line *ch*), where the solid ZW_9 decomposes into ZW_6 and solution saturated with this hydrate. During decomposition there are three phases present, so the temperature remains constant until all of the ZW_9 has been exhausted. Further heating causes more ZW_6 to dissolve until 20° is reached, when all of it will have passed into solution, and the system above this temperature consists of a single phase.

The hydrate $Zn(NO_3)_2.6H_2O$, or ZW_6, consists of 63.6 per cent by weight anhydrous zinc nitrate. A solution of this composition will exist above 36.5°, but if cooled to this temperature, will deposit pure ZW_6; point (*d*) therefore is the melting point of ZW_6. Addition of more Z will lower the melting point until point *j* is reached, which is the eutectic for ZW_6 and ZW_3.

Suppose a solution of 60 per cent Z were cooled at a uniform rate from 50° to $-$ 30°. By a uniform rate of cooling, a given number of calories per minute are withdrawn from the system; this may or may not produce a uniform fall of temperature, depending on whether phase changes are taking place or not. When 31° is reached, the solution deposits solid ZW_6, and the rate of temperature fall is less than when no solid was separating out. This solid continues to separate out until $-$ 17° is reached, which is a point on the line *hg*, and the transition temperature of ZW_6 to ZW_9. At this point ZW_9 forms from ZW_6 and solution until all of the solution is exhausted, when the field *khgr* is entered, and further cooling forms no new phases.

The behavior of this solution differs from that of a 50 per cent solution at $-17°$ in that a 50 per cent solution forms ZW_9 from ZW_6 and solution until all of the ZW_6 is exhausted, when some solution still remains. Further cooling therefore results in further deposition of ZW_9 and a decrease in the quantity of solution, which changes its composition along the line *cb* until point *b* is reached. Here ice and solid ZW_9 separate until all of the solution is exhausted.

The line *je* shows the solubility of ZW_3, and any system having a composition and temperature to bring it within the field *fje* consists of solution and pure solid ZW_3. As this solid contains more than 75 per cent anhydrous zinc nitrate, its composition line, corresponding to *hkp* for ZW_9 and *dgr* for ZW_6, does not appear on this diagram.

A solution containing 70 per cent Z when cooled would deposit ZW_3 at 42°, and continue to deposit this phase while the solution changed its composition along *je* until 35°, where the solid hydrates ZW_3, ZW_6 would both deposit until all of the solution was used up; the field *jfsr* would be entered, and further cooling would lead to the formation of no new phases. Systems such as this one of zinc nitrate and water may be studied by means of cooling curves, just as in the case of alloys. It should be noted that the separation of a phase upon cooling always takes place with the evolution of heat, hence with a decrease in the rate of temperature fall when heat is withdrawn from the system at a uniform rate. When an invariant point is reached, two phases are separating at once, and no change in the temperature of the system is produced by cooling until one of the phases has been exhausted.

Study Question.—Draw cooling curves for systems containing the following percentages of zinc nitrate, and write upon each portion of each curve the phases present: 0, 10, 20, 39, 42, 45, 50, 53.9, 60, 63.6, 70. Plot temperature vertically, time in arbitrary units horizontally, and note that an invariant system evolves heat without changing its temperature, until it ceases to be an invariant system.

Questions

1. From the data of Table 91 calculate the least quantity of hydrogen which will reduce a formula weight of silver sulfide to silver at 617°C. Calculate also the weight of silver required to react with a mixture of a mol of hydrogen and one of hydrogen sulfide to produce equilibrium in the presence of both solids at this temperature.

2. Calculate the heat of reaction between silver and hydrogen sulfide at 800° from the equilibrium constants. Calculate the temperature at which the equilibrium constant is 0.250 for this reaction.

3. Ten grams of silver sulfide remain in contact with a liter of hydrogen at 700° until equilibrium is established. (*a*) Calculate the equilibrium constant of the reaction at this temperature from the data given in the text. (*b*) Calculate the mol fraction of hydrogen sulfide in the gaseous mixture at equilibrium. (*c*) What is the least quantity of hydrogen which would reduce all of the silver sulfide to silver at this temperature?

4. Describe in detail, by reference to Fig. 38, what would happen if urethane at 35° and 5,000 atmospheres were allowed to expand slowly while the temperature remained constant. Do the same for a temperature of 100°.

5. Describe the changes in a system composed of urethane when it is cooled from 100° to 0° under constant pressures of 1 atmosphere, 2,500 atmospheres, 3,000 atmospheres, 3,500 atmospheres.

6. State what phases exist in each of the fields of Fig. 41.

7. State what phases exist in each of the fields of Fig. 43.

8. Metal *A* melts at 500°, *B* melts at 600°, and the compound formed by them, *AB*, melts at 1,000°. No solid solutions are formed. Draw a temperature-composition diagram showing in a general way the nature of this system, choosing reasonable points for the location of other characteristic points of the diagram for which data are not given. Draw through this diagram vertical lines at 5, 40 and 90 atomic per cent *A*, and at a minimum point in the diagram, and draw a curve showing the rate at which the temperature would rise through each of these portions of the diagram if heat was added at a uniform rate. These curves are called heating curves; breaks in them may be employed to show the character of any phase changes occurring during heating.

9. Potassium acid sulfate, $KHSO_4$, forms four solid phases and the triple points are as follows:

I–II–IV	199°	1,830 atmospheres
II–III–IV	118°	2,900 atmospheres

Phase III is stable at room temperatures and pressures and it changes to IV at about 48° and 6,000 atmospheres. The transition points under 1 atmosphere are 164 and 180°, and phases I and IV are in equilibrium at 220° and 2,500 atmospheres. (*a*) On a diagram covering the range 40 to 350° and 0 to 6,000 atmospheres, draw lines representing the equilibrium between the solid phases, and letter each field to show what phase is stable within it. (*b*) The melting point is 210° and the solid sinks in the liquid. Draw a very short line (0 to 200 atmospheres say) showing the equilibrium between liquid and solid, and show by exaggerating the slope of this line whether the melting point is raised or lowered with increase of pressure. (*c*) Tell in detail all that would happen if $KHSO_4$ were heated very slowly from 40 to 260° under a pressure of 2,500 atmospheres, but do not draw any conclusions which are not justified by the data given.

10. Phenol (m.p. 45°) and water form at 20° two liquid phases, one of which contains 5 per cent phenol; the other 90 per cent phenol. The two substances are miscible in all proportions at temperatures above 68°. (*a*) Draw a temperature-composition diagram for this system. (*b*) What would happen at 50° on adding successive small portions of phenol to water until the system was 99 per cent phenol? (*c*) What would happen on cooling a 50 per cent phenol solution from 80° to −25°? Describe the texture of the solid system. (*d*) Same as *c* for 1 per cent and for 99 per cent phenol solutions.

11. Bismuth (m.p. 267°) and tellurium (m.p. 426°) form a compound (m.p. 575°) containing 48 per cent of tellurium by weight. No solid solutions form; the two eutectic temperatures are 261 and 388°. Draw a temperature-composition diagram for this system and letter its fields. Draw cooling curves showing the behavior of melts containing 10, 40, 65 and 95 per cent tellurium when cooled from 600 to 200°. Indicate on each curve the phase which appears or disappears at each break in it. What would happen at 400° if tellurium is added gradually to bismuth, assuming equilibrium to be maintained at all times?

12. The system water up to pressures of 5,000 atmospheres and below 0° forms four solid phases and one liquid phase. The triple points are as follows for ice I, ice II, ice III, ice V and liquid:

I–III–liquid	−22°	2,100 atmospheres
I–II–III	−35°	2,130 atmospheres
III–V–liquid	−17°	3,500 atmospheres
II–III–V	−24°	3,500 atmospheres

(Ice IV does not appear on the diagram.)

Two phases only are present at −40° and 5,000 atmospheres; at −40° and 2,000 atmospheres; and at −10° and 5,000 atmospheres. Draw a sketch of the pressure-temperature diagram covering the range of 0° to −40° and 0 to 5,000 atmospheres. What conditions are represented by the line joining the two triple points at 3,500 atmospheres? What is the significance of the straight line joining −22° and 2,100 atmospheres to 0° and 1 atmosphere? Will ice V float or sink in the liquid in contact with it?

13. Naphthalene lowers the freezing point of phthalic anhydride as follows:

Mol per cent anhydride	0	8.07	15.3	21.7	26.1
Freezing point	80	75.1	71.2	67.3	64.9

and phthalic anhydride lowers the freezing point of naphthalene:

Mol per cent anhydride	100.	90.5	80.7	67.3	44.8	32.2	26.1
Freezing point	130.8	124.8	118.5	109.2	88.9	73.5	64.9

Construct from these data the temperature-composition diagram of the system and letter its fields to show what phases exist within them. No solid solutions form. (Monroe, *J. Ind. Eng. Chem.*, **11,** 1119 (1919).

14. Toluene-*o*-sulfonamide and the corresponding para-compound mix in the liquid state in all proportions, and each lowers the freezing point of the other as follows:

Per cent para compd	0	17.96	25.87	35.58	40.54	50.39	61.15	82.59	100.
Freezing point	156.3	145.5	139.7	133.6	130.3	120.8	110.4	126.8	137.5

Construct from these data the temperature-composition diagram. (McKie, *J. Chem. Soc. London*), **113,** 799 (1918).

15. Calculate the heat of reaction NH_4Br (solid) = $NH_3 + HBr + Q$ between 330 and 350°. *Ans.* About 26,000 cal. Calculate the total mols per liter at 350°, when the pressure is 237 mm. of mercury. *Ans.* 0.0048.

16. Hydrogen may be prepared by passing steam over hot iron and freezing out the remaining water. Assuming the reaction to be $Fe + H_2O = FeO + H_2$ at 1,100° calculate the number of mols of steam required to make a mol of hydrogen. The dissociation constants are $K_{FEO} = 2.5 \times 10^{-13}$ and $K_{H_2O} = 3.5 \times 10^{-13}$ at 1,100°.

17. What will be the composition of the gas phase in the previous problem if two mols of steam are heated with excess iron? How many mols of FeO will be formed?

18. Write the reaction which occurs when an excess of Ag_2CrO_4 is treated at 25° with 0.2 normal NaCl, and find the ratio $(CrO_4^{=})/(Cl^-)$ in the solution at equilibrium. The solubility product for Ag_2CrO_4 is 10^{-10} and that for AgCl is 1.2×10^{-10}. (*b*) By reference to this ratio discuss the accuracy of the end point in the Volhard titration for chloride in the presence of K_2CrO_4 indicator. (The end point is taken when Ag_2CrO_4 begins to precipitate.)

19. The solubility of benzoic acid in water at 25° is 0.026 formal. Calculate its solubility in 0.1 formal sodium acetate. $K_a = 1.8 \times 10^{-5}$ for acetic acid and 6.0×10^{-5} for benzoic acid.

20. The equilibrium constant of the reaction CuCl (solid) + Cl^- = $CuCl_2^-$ is 0.066 at 25° and 0.314 at 75°. Calculate the heat of solution of CuCl in dilute HCl. *Ans.* 6,440 cal. absorbed per mol of CuCl.

21. Experiments on the solubility of zinc carbonate in water containing carbon dioxide in excess gave the following results at 25°, in mols per liter of solution.

TOTAL CO_2	TOTAL ZINC	IONIZATION OF $Zn(HCO_3)_2$
0.1839	0.00211	0.90
0.4538	0.00291	0.89
0.7678	0.00343	0.88

(*a*) Calculate the equilibrium constant of the reaction $ZnCO_3$ (solid) + H_2CO_3 = $Zn(HCO_3)_2$ at 25°. (*b*) The ionization constants of carbonic acid at 25° are $K_1 = 3.5 \times 10^{-7}$, $K_2 = 4.0 \times 10^{-11}$. Calculate the solubility product of zinc carbonate and the molal solubility of it in water on the assumption of no hydrolysis. (*c*) Calculate the solubility of zinc bicarbonate (*i.e.*, total zinc) in 0.25 formal carbonic acid solution. (The cubic equation so obtained is best solved by estimating a value of S, substituting it in the equilibrium expression, and by trial determining whether the value is too high or too low, estimating a new value, and repeating until a value is found which satisfies the equation.)

Ans. (*a*) 3.8×10^{-10}; (*b*) 4.6×10^{-6} mols per liter; (*c*) 0.0024 molal.

22. The solubility of silver acetate in water at 16° is 0.060 formal. Calculate its solubility in 0.10 formal silver nitrate solution. (Make an estimate of the fractional ionization from that of other salts of similar type at the same concentration.)

24. The solubility of thallous chloride in water at 25° is 0.0161 formal. Calculate its solubility in 0.025 normal solutions of HCl, KCl, and Tl_2SO_4 by means of the solubility product law, and compare these calculated solubilities with the experimental ones given in Table 95.

CHAPTER X

KINETICS OF REACTIONS

General Law.—The familiar reactions of inorganic chemistry proceed to completion almost instantly in many cases, but some of these reactions, and almost all of those of organic chemistry require a measurable amount of time. When a one-way reaction is concerned, it approaches completion at a decreasing rate; when a reversible reaction is concerned, it approaches its equilibrium point at a decreasing rate. As a provisional statement of the law governing reaction rates, we may say that the rate at which any substance reacts is proportional to its concentration at the moment.

First Order Reactions.—To take as an example a reaction in which the concentration of only one substance is decreasing, sugar reacts with water in dilute solution to form glucose and fructose at a rate which is proportional to the sugar concentration. This rate is proportional to the water concentration as well, but the latter remains essentially unchanged throughout the reaction in a dilute solution. When half of the sugar originally present has been hydrolyzed, the rate of hydrolysis (mols per liter per minute) is half that of the reaction rate at the first instant when sugar was put into water. A reaction rate may also be defined as the rate at which the concentration of any reaction product is increasing. Let C denote the concentration of any reaction product, and C_0 the concentration of the reacting substance at the moment the reaction started. Then at any time, the concentration of reacting substance is the difference between that present at the start and that used in the reaction, or $(C_0 - C)$. In the reaction

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6,$$

the concentration of sugar when the elapsed time is 0 is C_0, that after the time t is $(C_0 - C)$, and the concentration of glucose or fructose is C. The rate at which C is increasing is dC/dt, and this is the rate of the reaction:

$$\frac{dC}{dt} = k(C_0 - C). \qquad (1)$$

This is the expression for the velocity of any reaction in which only one reacting substance is changing its concentration, that is, when there is only one molecule of reacting substance involved in the chemical equation. The *order* of a reaction is the number of molecules of reacting substance involved in the chemical equation which change their concentration during reaction. For example, the reaction of hydrogen iodide to form hydrogen and iodine is written

$$HI + HI = H_2 + I_2,$$

since two molecules of hydrogen iodide are required to form one molecule of hydrogen. This is a *second order* reaction, and equation (1) above will not describe its velocity. In the sugar equation, two molecules are involved, but only one is changing its concentration. The order of a reaction is the number of molecules of reacting substance which *change concentration* during this reaction.

Catalysers.—Substances which accelerate a reaction without appearing in the equation for it and without being changed by the reaction are called catalysers. Acids increase the velocity of sugar hydrolysis but are not changed in concentration by the reaction; so, to a smaller extent, do bases. Fine platinum powder (platinum black) accelerates many gaseous reactions, but remains unchanged by them, yeasts and enzymes increase the velocity of fermentation and of digestive processes by catalysis. Often the manner of this aid in reaction is completely unknown; in a few cases it has been shown that the catalyser reacts with some of the reacting substances, forming an intermediate product, which then reacts with the remaining substances to regenerate the catalyser and complete the reaction. In other cases the mere presence of a catalyser accelerates a reaction when no intermediate product can be discovered. It is likely that solid catalysers adsorb gaseous or dissolved reacting substances on their surfaces in a higher concentration than exists in the bulk of reacting mixture, and discharge the products into the reaction space, but this explanation is doubtless incomplete for many reactions. Usually the accelerating effect is proportional to the surface of catalyser exposed to a reacting mixture.

Sugar Hydrolysis.—The hydrolysis of sugar at any temperature is accelerated by the presence of acids (hydrogen ions), and the extent of this increased velocity is proportional to the hydrogen ion concentration. Thus for this reaction we may write

$$\frac{dC}{dt} = k(\mathrm{H}^+)(C_0 - C)$$

where k is the reaction constant or proportionality constant. (H^+), the hydrogen ion concentration, is also a constant for any given experiment, since the catalyser concentration is unchanged, and we may write these two constants as one single constant K,

$$\frac{dC}{dt} = K(C_0 - C),$$

which is the first-order equation; but we must remember that K is now dependent upon the hydrogen ion concentration, and that in applying the equation to experimental data, agreement between calculation and experiment is not to be expected if the acid concentration is not the same throughout a series of experiments. Separating the variables and integrating between the limits $t = 0$ and any time t, the corresponding limits for C, the concentration of reaction product at any instant being 0 and C, we have

$$\frac{dC}{(C_0 - C)} = \frac{-d(C_0 - C)}{(C_0 - C)} = Kdt,$$

$$\ln \frac{C_0}{(C_0 - C)} = Kt \quad \text{or} \quad 2.303 \log \frac{C_0}{(C_0 - C)} = Kt. \qquad (1a)$$

The integral just given was obtained by integrating between the limits $t = 0$, when $C = 0$, and the concentration C at the time t. If it is desired to calculate the concentration at one time from that at another, this equation may be integrated between t_1 and t_2, for which the equation is as follows:

$$2.303 \log \frac{C_0 - C_1}{C_0 - C_2} = K(t_2 - t_1)$$

where C_1 and C_2 correspond to the concentration of reaction product at t_1 and t_2 respectively.

It is often convenient to express the extent of a reaction at a given time as the fraction of reacting substance decomposed, x. Since in the equation one molecule of sugar forms one of glucose, C mols of sugar have been decomposed when C mols of glucose have formed, and the fraction which has reacted is therefore $\frac{C}{C_0} = x$. Upon dividing both numerator and denominator of the fraction in equation (1a) by C_0 we obtain

$$2.303 \log \frac{1}{1 - x} = Kt. \tag{1b}$$

This equation will be useful in calculating reaction constants from experimental data.

The velocity of sugar hydrolysis is generally followed by observing the change in optical rotatory power of the solution. For when a beam of plane-polarized light is passed through a sugar solution, its plane of vibration is rotated toward the right through an angle proportional to the concentration of sugar in solution; polarized light is rotated in the opposite direction by the products of sugar hydrolysis. As the sugar concentration decreases, and that of the reaction products increases, the plane of rotation is changed, and the fraction of sugar decomposed is readily calculated for any time, since it is the ratio of the change in rotation up to that time divided by the total change in rotation when the reaction is completed. Let α_0 and α_f represent the initial rotation and final rotation, respectively, and let α_t represent the rotation at any time t. Then x, the fraction of sugar decomposed at t, is $\frac{\alpha_0 - \alpha_t}{\alpha_0 - \alpha_f}$. Substituting this value of x in equation (1b), and combining the catalyser concentration with the factor 2.3 (logarithmic conversion factor) in the constant of reaction, leads to the following expression for the reaction constant in terms of observed rotations:

$$K = \frac{1}{t} \log_{10} \frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}.$$

Table 101 shows the results of experiment at 30° on sugar solutions in which the catalyser is 2.50 formal formic acid. It will be observed that the values of K are constant, and independent of the sugar concentration or the extent to which the reaction has progressed.

TABLE 101.—SUGAR HYDROLYSIS AT 30° IN 2.5 MOLAL FORMIC ACID[1]

Initial sugar concentration 0.44 molal			Initial sugar concentration 0.167		
Elapsed time (hours)	Rotation of plane of light	$K = \frac{1}{t}\log\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$	Elapsed time (hours)	Rotation of plane of light	$K = \frac{1}{t}\log\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$
0	(57.90)	......	0	(22.10)	
2	53.15	0.0146	2	20.30	0.0146
4	48.50	0.0149	5	17.85	0.0145
6	44.40	0.0147	10	14.15	0.0148
8	40.50	0.0147	15	11.10	0.0147
11	35.20	0.0146	20	8.65	0.0145
15	28.90	0.0146	26	6.00	0.0146
21	20.70	0.0146	30	4.50	0.0147
27	13.50	0.0149	39	1.90	0.0146
35	6.75	0.0148	45	0.35	0.0149
40	3.40	0.0147	59	−1.80	0.0146
46	− 0.40	0.0149	73	−3.20	0.0148
52	− 2.95	0.0148	94	−4.30	0 0147
66	− 7.45	0.0146	133	−5.10	0.0147
85	−11.25	0.0146	Complete	−5.50	
112	−13.80	0.0147			
Complete	−15.45				

Another reaction of the first order is the conversion of hydroxyvaleric acid into valerolactone in the presence of an acid catalyser,[2] the reaction being followed by titrating samples removed at intervals. As the reaction proceeds, hydroxyvaleric acid disappears and the titration of a sample of definite volume requires less and less standard alkali. Complete reaction corresponds to titrating the catalyser only; hence the fraction of hydroxyvaleric acid decomposed at a time *t* is obtained by subtracting the volume of alkali used at that time from the volume employed in the initial titration, and dividing this difference by the difference between the first titration and that corresponding to complete reaction. The alkali concentration need not be known. Two series of experiments are shown in the following table.

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[1] Rosanoff, Clark and Sibley, *J. Am. Chem. Soc.*, **33**, 1,911 (1911).

[2] Taylor and Close, *J. Am. Chem. Soc.*, **39**, 422 (1917).

TABLE 102.—CONVERSION OF HYDROXYVALERIC ACID INTO VALEROLACTONE BY 0.025 NORMAL HYDROCHLORIC ACID AT 25°

Time, minutes	Titration, cubic centimeters	10^4K	Time, minutes	Titration, cubic centimeters	10^4K
0	19.04	.....	0	18.55	
48	17.60	17.2	46	17.11	17.1
76	16.90	17.0	125	15.18	17.1
124	15.80	17.2	174	14.22	17.2
204	14.41	17.3	221	13.49	17.2
238	13.94	17.3	262	12.97	17.1
289	13.37	17.15	307	12.45	17.2
Complete	10.71	.....	Complete	9.87	

Here, as in other cases where a catalyser is employed, the reaction constant as calculated above includes the concentration of catalyser in the reaction constant. These experiments were repeated under exactly similar conditions except that the hydrochloric acid concentration was varied, and it was found that the velocity constant is proportional to the acid concentration, with only a slight variation. The figures obtained are shown in Table 103.

TABLE 103.—CATALYSER CONCENTRATION AND VELOCITY CONSTANT

Concentration of catalyst	10^4K	Ratio
0.10N	67.7	677
0.05	34.3	686
0.025	17.14	686
0.010	6.83	683

At higher acid concentrations the proportionality is not so good, and the explanation is not definitely known. Some authorities assert that hydrogen ions act as the catalyst, and in some reactions a better ratio of reaction constant to catalyst is obtained when a correction for incomplete ionization of the acid is applied; but cases are known where this does not remove the difficulty. A separate catalytic effect due to the non-ionized acid molecules has been postulated to explain the data, and is doubtless responsible for some of the observed effects. A full explanation of catalysis is yet to be discovered.

Second Order Reactions.—When a reaction depends upon a collision between two molecules, the reaction is of the second order, whether the two reacting molecules are of the same kind or of different kinds. Thus the decomposition of hydrogen peroxide according to the equation

$$2H_2O_2 = 2H_2O + O_2$$

is a second order reaction, and the velocity of it is proportional to the square of the hydrogen peroxide concentration at any instant. Our provisional statement of the law of reaction velocity may now be modified as follows: *The rate at which each substance reacts is proportional to its concentration, raised to the power which is its coefficient in the chemical equation.* While a mol of hydrogen peroxide can decompose into water and oxygen, a single molecule cannot so decompose, for it cannot form half of a molecule of oxygen. Two molecules of hydrogen peroxide give one of oxygen, hence the reaction is of the second order. The equation for its rate is

$$\frac{dC}{dt} = k(C_0 - C)^2 \qquad (2)$$

which upon integration becomes

$$\frac{C}{(C_0 - C)C_0} = kt \qquad (2a)$$

if the integration limits are zero time to the time t, corresponding to zero and C for the concentration of the product formed. Upon dividing both numerator and denominator of the fraction by C_0, and noting that C/C_0 is x, the fraction decomposed, we have

$$\frac{x}{1 - x} = ktC_0. \qquad (2b)$$

In treating any given set of experimental data, the constants

k and C_0 may be combined into a single constant K, if desired. In Table 103 are shown the results of applying this equation to experimental data.[1] Under K_1 the "constant" obtained by applying equation (1) is given, under K_2 is shown that from application of the proper equation for a reaction of the second order. It will be seen at once that K_2 is practically constant throughout the experiment, while K_1 decreases to half its original value in less than forty minutes, showing that the reaction is not of the first order.

TABLE 103.—RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE IN SOLUTION IN QUINOLINE

(A Small Quantity of Manganese Acetate has been Added to Accelerate the Reaction.)

Time, minutes	Cubic centimeters oxygen evolved	K_1	K_2
4.9	11.8	0.0693	0.00178
6.6	14.3	0.0649	0.00177
9.2	18.0	0.0626	0.00183
11.7	20.7	0.0598	0.00185
18.9	25.7	0.0506	0.00181
22.5	27.4	0.0487	0.00179
27.3	29.5	0.0461	0.00183
30.8	30.2	0.0431	0.00175
32.1	31.2	0.0384	0.00188
Complete decomposition	41.2		Average 0.00181

The law for reaction velocity when a molecule of one substance and one of another react is the same, that is, the velocity of reaction is proportional to the concentration of each substance, therefore to the product of the concentrations. If we denote by C_a and C_b the original concentrations of two reacting substances, and by C the concentration of a reaction product, the concentrations at any moment are $(C_a - C)$ and $(C_b - C)$, and the velocity equation is

$$\frac{dC}{dt} = k(C_a - C)(C_b - C) \tag{3}$$

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[1] Walton and Jones, *J. Am. Chem. Soc.*, **38**, 1,959 (1916).

for which the integral is

$$\frac{2.303}{(C_a - C_b)} \log \frac{C_b(C_a - C)}{C_a(C_b - C)} = kt. \tag{3a}$$

This equation cannot be transformed into one expressing the fraction of reacting substance used at any time unless the two starting concentrations C_a and C_b are equal, for the reaction uses equal mols of each, and when (for example) 0.1 mol of each has been used, this is not the same fraction of C_a as of C_b. If C_a is equal to C_b, equation (3) becomes identical with (2), and its integral is (2*a*) or (2*b*).

The reaction between an ester and sodium hydroxide proceeds at a rate which is proportional to the product of the ester concentration and the base concentration. Reaction constants for this case are shown below in Table 104, corresponding to the reactions

$$CH_3CO_2CH_3 + NaOH = CH_3OH + NaCOOCH_3$$

and

$$C_2H_5COOCH_3 + NaOH = C_2H_5OH + NaCOOCH_3.$$

The esters and alcohols are not ionized and do not therefore conduct the electric current; measuring the conductivity of the reaction mixture therefore shows the extent to which sodium hydroxide has been replaced by the poorer conductor, sodium acetate. If the reacting substances are present in equivalent quantity, complete reaction corresponds to complete replacement of hydroxyl ion (equivalent conductance at 25°, 192) by acetate ion (equivalent conductance 40.8); that is, a change from a conductivity proportional to the conductances of sodium and hydroxyl ions ($50.9 + 192 = 242.9$) to one proportional to the conductances of sodium and acetate ions ($50.9 + 40.8 = 91.7$), or a decrease of over 60 per cent. The fraction of sodium hydroxide changed to acetate at any moment is therefore $(L_0 - L_t)/(L_0 - L_f)$, where the symbols represent the initial, temporary and final observed specific conductances. Using this method of measuring reaction velocities, the following data have been obtained for solutions which at the start were 0.01 formal in sodium hydroxide and 0.01 formal in ester.[1]

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[1] Walker, *Proc. Royal Soc. London* (*A*) **78**, 157 (1906).

TABLE 104.—SAPONIFICATION OF ESTERS AT 25°

Ethyl acetate			Methyl acetate		
Time, minutes	Fraction saponified	$K = \frac{1}{t} \cdot \frac{x}{1-x}$	Time, minutes	Fraction saponified	$K = \frac{1}{t} \cdot \frac{x}{1-x}$
5	0.245	0.0649	3	0.260	0.117
7	0.313	0.0651	5	0.366	0.115
9	0.367	0.0645	7	0.450	0.117
15	0.496	0.0650	10	0.536	0.115
20	0.566	0.0652	15	0.637	0.117
25	0.615	0.0642	21	0.712	0.118
33	0.680	0.0644	25	0.746	0.118

Reactions of Higher Orders.—Let the general equation for a reaction of any order be

$$aA + bB + eE + \ldots = \ldots;$$

then the velocity expression for this reaction is

$$\frac{dC}{dt} = k(C_a - C)^a(C_b - C)^b(C_e - C)^e \ldots \qquad (4)$$

where C is the concentration of the reaction product. No general integral for this equation can be given. For a third order reaction where the starting concentrations are equal, the equation becomes

$$\frac{C_0^2 - (C_0 - C)^2}{C_0^2(C_0 - C)^2} = 2kt \qquad (5)$$

or, in terms of the fraction of each substance used at any time, when all of the initial concentrations are equal,

$$\frac{x(2 - x)}{(1 - x)^2} = 2ktC_0^2 = Kt. \qquad (6)$$

The reaction between nitric oxide and oxygen,[1]

$$2NO + O_2 = 2NO_2,$$

is of the third order, since it involves two molecules of nitric oxide and one of oxygen. By treating an extended series of measurements according to equation (5) it was found that K, the reaction constant, is 36.3 at 0°, 25 at 25°, 17.6 at 50°, and 11.2 at 86°. The constants obtained at any one temperature were very concordant, showing that equation (5) represents the true law of reaction velocity, and that this reaction is one involving three molecules.

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[1] Wourtzel, *Compt. rendus*, **170**, 229 (1920).

Mechanism of a Reaction.—When the equations given above are applied to chemical reactions, cases are encountered in which the "order" of a reaction is not that to be expected from its chemical equation. As there is ample confirmation of the truth of the equations, the reactions under consideration must take place in steps. Thus suppose a given reaction to be taking place in two steps, of which the first was measurably slow and the second was practically instantaneous; observations would show the velocity of the first step alone. A case in point is the reaction

$$2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + H_3PO_4 + 2HCl$$

which appears to be of the third order, since the water-concentration does not change. Experiments[1] show that this process takes place in two steps, of which the first is the time-reaction and the second is fast enough to remove the products of the first almost instantly. The first step is

$$HgCl_2 + H_3PO_3 = HgCl + HCl + H_2PO_3$$

which is followed by the very fast reaction

$$2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4.$$

Such velocity experiments therefore throw light on the actual process by which a chemical reaction occurs, while the chemical equation shows only the final result of the process.

Reversible Reactions.—The equations given above apply equally well to reversible reactions. Thus the velocity of the reaction $N_2O_4 = NO_2 + NO_2$ is proportional to the concentration of nitrogen tetroxide,

$$\frac{dC}{dt} = k_1(C_0 - C);$$

and velocity of the reverse reaction, $NO_2 + NO_2 = N_2O_4$, is proportional to the square of the concentration of NO_2,

$$\frac{dC'}{dt} = k_2(C_0' - C')^2.$$

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[1] Linhart, *Amer. Chem. J.*, **55**, 354 (1913).

At equilibrium these velocities must be equal, since no change in the concentration of any molecular species is observed. Upon equating them, and writing for $(C_0 - C)$ its equal (N_2O_4), and for $(C_0' - C')$ its equal (NO_2), we have

$$\frac{dC}{dt} = \frac{dC'}{dt} \quad \text{or} \quad k_1(N_2O_4) = k_2(NO_2)^2,$$

whence

$$\frac{(NO_2)^2}{(N_2O_4)} = \frac{k_1}{k_2} = K,$$

which is the mass action expression for the chemical equation $N_2O_4 = 2NO_2$. This discussion should not be considered as a "derivation" of the law of mass action, but merely a demonstration that apparently stationary equilibrium is not incompatible with a finite velocity of reaction in each direction.

Suppose a general reversible reaction to be $a + b = c + d$, and consider that we start with a and b present at equal concentrations. Then the initial rate of this reaction is the rate at which the concentration of c or d is increasing. As soon as any c and d have been formed, the reverse reaction by which they re-form a and b can commence. As the concentrations of c and d are small at first, while those of a and b are comparatively much larger, the reaction proceeds rapidly toward the formation of more c and d. With increasing concentrations of these substances, the reverse rate increases; while with increasing concentrations of c and d, the rate of their formation from a and b decreases. After a time the reaction rates are equal, and equilibrium is reached. At equilibrium, each reaction is proceeding independently, but the concentrations are not changing, because the reaction rates are equal.

Effect of Temperature.—Nearly all chemical reactions proceed more rapidly at higher temperatures than at lower ones. The general effect consists in doubling the velocity for a rise in temperature of about 10°, though in some cases the speed is multiplied by 2.5 or even 3.5 for a rise of 10°. Many biological reactions have a maximum velocity at some characteristic temperature, but it is not certain that the decreased velocity at higher temperatures is a chemical effect. Excluding these from consideration, the rate of change of velocity is that stated above. An equation expressing this change in the velocity constant for any particular reaction, due to van't Hoff, is

$$\frac{d \ln k}{dT} = \frac{A}{T^2}.$$

The usefulness of this equation is much restricted, since the constant A must be determined from experiment for each reaction at two different temperatures. It is of service in interpolating for temperatures between those represented in a series of experiments, where the constant A may be evaluated from data at any two temperatures after the equation is integrated between limits. The method of integration is the same as that for the Clapeyron equation on page 74, and the integrated form is

$$\ln \frac{k_2}{k_1} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

To illustrate the use of this equation, refer to the reaction constants for nitric oxide oxidation, page 307; let 36.3 and 273° absolute correspond to k_1 and T_1, and 25 at 298° absolute, correspond to k_2 at T_2. Substitution into the above equation leads to $A = -1{,}165$. By means of this value the reaction constant for 50° may be calculated from that at 25° to be 18.0; the measured value of the reaction constant at 50° is 17.6. However, this value of A is applicable only to the reaction in question, not at all to some other reaction over this temperature range.

Another test of this equation may be based on the monomolecular reaction[1] of which the result is

$$N_2O_5 = N_2O_4 + 1/2\ O_2,$$

though it is probable that the reaction takes place in steps. However, the experimental data show conclusively that the reaction is a monomolecular one. In Table 104*a* are given the reaction constants at various temperatures, together with those calculated by van't Hoff's equation from the experimental value at 25°. The numerical value of A is 24,790 for this reaction.

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[1] Daniels and Johnston, *J. Am. Chem. Soc.*, **43,** 53 (1921).

Temperature	10^3K	
	Observed	Calculated
0°	0.047	0.0444
25	2.03	......
35	8.08	7.9
45	29.9	28.3
55	90.0	93.2
65	292.	286.

Another expression for calculating the specific reaction constant at one temperature from that at some other temperature[1] may be written

$$\frac{k_1}{k_2} = \left(\frac{T_1}{T_2}\right)^m$$

where T_1 and T_2 are the absolute temperatures corresponding to the reaction constants k_1 and k_2, and m is 28.5. This equation was found to express the change of velocity with temperature for a variety of reactions. The reaction rate at 10° is 2.78 times that at 0°; the rate at 20° is 7.46 times that at 0°; and the rate at 30° is 19.3 times that at 0°.

Questions

1. A solution 0.167 molal in sugar has at 30° a rotation of 22.10°. Owing to the presence of acid in the solution, inversion takes place at such a rate that the angle of rotation of polarized light is 11.10° after 15 hr. and 0.35 after 45 hr. (*a*) Calculate the angle of rotation corresponding to complete inversion of the sugar. (*b*) Calculate the time necessary for half of the sugar to be inverted. (*c*) The solution was 2.50 formal in formic acid, whose ionization constant is 2.10×10^{-4}. Calculate the hydrogen ion concentration in this solution, and estimate the time required for inverting half of the sugar when the catalyzing acid is 0.10 formal hydrochloric acid, which is 92 per cent ionized.

2. In a solution containing 0.1 mol of ethyl acetate and 0.1 mol of sodium hydroxide per liter, 10 per cent of the ester is decomposed in 15 min. at 10° and 20 per cent at 25°. How much would be decomposed in 5 min. at 55°?

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[1] Harcourt, *Phil. Trans. Roy. Soc. London*, **212**, 187 (1913).

3. A solution of sugar in 0.002 normal hydrochloric acid has at 40° a rotation of 22.28°. In 90 min. this has decreased to 19.77°, in 150 min. to 18.27°, in 210 min. to 16.83°, and after the inversion was complete, to −5.37°. Calculate the reaction constant. Calculate the rotation of the solution when the reaction had proceeded 3 hr. How long would it take for the rotation to become 0°?

4. How long would it take to convert 40 per cent of hydroxyvaleric acid into valerolactone at 25° in the presence of 0.075 normal hydrochloric acid? See the text for data.

CHAPTER XI

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

Much careful work has been done in an effort to express the physical properties of substances (such as density or molal volume, optical properties, capillarity) in terms of figures representing the constituent atoms. Where these attempts have met with success, a value is assigned to each atom, and by adding together all of the values for each atom in the compound, each taken the number of times that it occurs in the formula for the substance, a measure of the desired property is obtained. It may be said at once that the fruitfulness of this type of work has scarcely justified the expenditure of time upon it, except in a very few cases. Thus the differences in several properties in passing from member to member of an homologous series are often quite constant, and useful relations among the members of a single group of elements such as the alkali metals or the halogens are known in a few cases. But nothing approaching a complete solution of the relation of physical properties to molecular constitution in general has yet been discovered. Some of these relations are mentioned briefly in this chapter.

Additive Properties.—Mass is an example of a strictly additive property; the molecular weight of a substance is exactly the sum of weights of the constituent atoms. Volume is sometimes roughly an additive property, though some astonishing exceptions are known; heat capacity is nearly additive in most cases. In general, an additive property is one which may be computed from the number of atoms of each kind and from a figure assigned to each atom which expresses its effect in all cases.

Constitutive Properties.—All properties which are not additive are said to be influenced by chemical constitution. A few properties, such as optical rotatory power, are the effect of constitution alone; and only these properties are properly considered under such a heading. Properties which are both additive and constitutive generally require further investigation.

Outside the field of organic chemistry constitutive influences have scarcely been studied at all; within this field they are properly the concern of the organic chemist, and the student is referred to organic chemistry text books for a consideration of optical activity.

Molecular Volumes.—If no expansion or contraction took place during chemical combination, the molecular volume of any substance could be computed by adding together the atomic volumes of its elements, and a ready means of computing the density would be available, since density is molecular weight divided by molecular volume. But the problem is not so simple; molecular volumes are far from additive properties in many cases. Thus the volume of a formula weight of cæsium chloride is about 30 c.c. smaller than the volume of the uncombined metal alone. But the difference between the molecular volume of a cæsium salt and the corresponding rubidium salt is roughly constant, indicating that the effective atomic volume of cæsium in its compounds is about the same for all compounds, even though it is not that of the uncombined element. The approximate constancy of this atomic volume for salts of the alkali metals is shown in the following table.

TABLE 105.—MOLAL VOLUMES OF SOLID HALIDES

	Cl	DIF.	Br	DIF.	I
Li	20.5	*4.6*	25.1	*7.9*	33.0
Dif.	*6.5*		*8.0*		*7.9*
Na	27.0	*6.1*	33.1	*7.8*	40.9
Dif.	*10.5*		*10.2*		*12.3*
K	37.5	*5.8*	43.3	*9.9*	53.2
Dif.	*5.7*		*6.1*		*6.6*
Rb	43.2	*6.2*	49.4	*10.4*	59.8
Dif.	*−0.8*		*−1.5*		*−2.2*
Cs	42.4	*5.5*	47.9	*9.7*	57.6

In the case of organic compounds, somewhat simpler volume relations are found, for the variations in chemical affinity, as measured by contraction during combination, are much smaller. Thus a beginning could be made by studying the difference in molecular volumes of members of homologous series, to obtain an average effective molecular volume for the —CH_2— group; then the effect of hydrogen could be determined by reduction at a double bond, the difference between an atomic volume of hydrogen and one of combined chlorine could be measured by the increase of volume attending substitution, etc. From such a procedure it has been found that the effective atomic volume of a carbon atom is 14.8 c.c., hydrogen 3.7, sulfur 25.6 (22 in rings), nitrogen 15.6 (10.5 in primary amines, 12.0 in secondary amines), chlorine 24.6, bromine 27, iodine 37 c.c. per atomic weight.[1] By adding together these volumes, each taken the number of times the atom occurs in a compound, a fair measure of its molecular volume is obtained. Such a procedure is somewhat uncertain,[2] as may be seen from the figures given by another investigator. The molecular volume of an aliphatic compound at its boiling point is

$$V = 10.5\,N_C + 5.25\,N_H + 10.5\,N_O + 0.25\,(N_C - 2)^2$$

As higher members of homologous series are considered, the molecular volume approaches as a limit that of $(CH_2)_n$. From the figures first quoted above, the volume of one CH_2 group is $14.8 + 7.4 = 22.2$, and the density should therefore approach $14/22.2 = 0.63$, but the limit actually approached is 0.86. We may calculate from the second set of figures the density of nonyl alcohol, $C_9H_{20}O$, as $144/220 = 0.65$; the experimental value being 0.84. Thus it is seen that no very satisfactory solution of this problem has been reached. Still another set of atomic volumes has been computed,[3] carbon 11; hydrogen 5.5; chlorine 22.8; carbonyl oxygen, 12.2; hydroxyl oxygen 7.8 c.c. per atomic weight. Densities calculated from molecular volumes based on these figures are, however, considerably in error. Thus acetone should have a molecular volume $33 + 33 + 12.2 = 78.2$, and a density of $58.1/78.2 = 0.74$; experiment gives 0.792. Chloroform should have a molecular volume according to these figures of $11 + 5.5 + 3 \times 22.8 = 84.9$ and a density of $119.4/84.9 = 1.40$, while experiment gives 1.52. From these figures the density of $(CH_2)_n$ which high members of homologous series should approach is $14/22 = 0.635$, which is greatly in error.

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[1] Gervais LeBas has studied the volume relations of organic compounds in detail. A large volume describes the results (Monographs on Physical Chemistry), of which the averages are here quoted.

[2] Kaufmann, *Z. Elektrochemie*, **25**, 343 (1919).

[3] Smiles, *Relation of Constitution to Physical Properties*, page 112.

Molecular volumes are not generally additive. They appear to be approximately so in the case of organic compounds on account of the nearly constant attraction exerted. Thus the volume of an atomic weight of oxygen in an organic compound varies from 4.7 to 12.0 c.c., depending upon its linking. The atomic volume of magnesium is 14 c.c., the molecular volume of magnesium oxide is 12 c.c., leading to the absurd conclusion that oxygen has a negative molecular volume.[1]

Molal Solution Volumes.—The change in volume which occurs upon solution of a substance has been investigated by many workers. When a salt dissolves in water, it is freed from the forces which hold it together as a solid, it dissociates into ions (for which the change in volume is only slight), and it has an opportunity to combine with some of the solvent. In the following table, the decrease in volume attending the formation of a salt from its elements plus that which occurs when it dissolves in water to form a normal solution at 25° is shown. This decrease in volume in a dilute solution is the volume change when the ions are formed from the elements; in a strong solution the volume change upon union of the ions is included, but this is shown to be small from the fact that the effective solution volume is nearly independent of concentration up to five molal solutions for alkali halides.

TABLE 106.—VOLUME CONTRACTION ATTENDING THE FORMATION OF A SOLUTION FROM WATER AND THE CONSTITUENT ELEMENTS OF THE SALT[2]

	Cl	DIF.	Br	DIF.	I
Li	19.6	*6.2*	13.4	*11.0*	2.4
Dif.	*10.6*		*10.7*		*10.6*
Na	30.2	*6.1*	24.1	*11.1*	13.0
Dif.	*11.4*		*11.3*		*11.2*
K	41.6	*6.2*	35.4	*11.2*	24.2
Dif.	*5.2*		*5.3*		*5.4*
Rb	46.8	*6.1*	40.7	*11.2*	29.6
Dif.	*7.9*		*8.0*		*8.2*
Cs	54.7	*6.0*	48.7	*11.4*	37.3

It will be noted that the difference between the molal solution volumes of the different chlorides and bromides is about 6.1 c.c., regardless of the alkali element; and that the difference between the solution volumes of lithium salts and corresponding sodium salts is 10.6 c.c. regardless of the halide. This indicates that the effective solution volume is an additive one for the two constituent ions of a salt. This is found to be the case, and the contraction per formula weight when a normal solution is formed may be distributed among the separate ions as shown in Table 107. From these values, it is possible to compute the volume contraction when a solution is formed from the elements of the salt and the contained water, merely by adding together the effects for the separate ions which result. It should be made clear that these contractions are not those observed when the salt is dissolved; they are the sum of two effects of which solution is the second, and formation of the salt from its elements the first.

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[1] For a full discussion of changing atomic volumes see Richards, *Proc. Am. Acad.*, **37**, 1,397 (1901); *J. Am. Chem. Soc.*, **36**, 2417 (1914).

[2] Baxter and Wallace, *J. Am. Chem. Soc.*, **38**, 98 (1916).

TABLE 107.—VOLUME CONTRACTION ATTENDING THE FORMATION OF A MOLAL SOLUTION; EFFECT OF THE SEPARATE IONS AT 25°

Ion formed	Contraction, cubic centimeters per atomic weight	Ion formed	Contraction, cubic centimeters per atomic weight
Li^+	11.4	Cl^-	19.1
Na^+	12.4	Br^-	12.7
K^+	24.0	I^-	1.4
Rb^+	29.1		
Cs^+	37.2		

Molecular Refraction.—This may be defined as the product of molecular weight and specific refraction, $M(n - 1)/d$, where M is the molecular weight, n is the index of refraction, and d is the density of the liquid. For organic substances it has been found that this molecular refraction is approximately the sum of atomic refractions, *i.e.*, values assigned to each element such that the sum of the values (each atomic refraction being multiplied by the number of atoms of the element in the molecule under consideration) gives the molecular refraction. For example, let us calculate the atomic refractions for carbon, R_C, and hydrogen, R_H, from the measured molecular refractions of pentane (25.23) and hexane (29.84). If atomic refractions are additive, the molecular refraction for pentane, whose formula is C_5H_{12}, should be $5R_C + 12R_H = 25.23$; that of hexane should be $6R_C + 14R_H = 29.84$; both of these equations are satisfied if R_H is 1.06 and R_C is 2.49. From similar calculations upon a large number of compounds, the average values $R_C = 2.490$ and $R_H = 1.066$ have been obtained;[1] the increment for each CH_2 group on ascending an homologous series is $R_{CH_2} = 4.622$. What value to assign to oxygen depends upon its linking in a compound; 2.137 for a ketone oxygen, 1.494 for hydroxyl oxygen (alcohols), 1.663 for ethereal oxygen. Some illustrations of the exactness of this law of additive refractions are given in Table 108, where the calculated molecular refractions are based on the average atomic refractions just given. In unsaturated compounds an effect is assigned to the double bond which is treated as an atomic refraction and added to the other atomic refractions.

TABLE 108.—MOLECULAR REFRACTIONS OF ORGANIC COMPOUNDS

Substance	Formula	Molecular refraction		Difference, per cent
		Measured	Calculated	
n-Pentane	C_5H_{12}	25.23	25.24	0.04
n-Octane	C_8H_{18}	39.16	39.11	0.13
Cyclopentane	C_5H_{10}	23.12	23.11	0.04
Acetone	CH_3COCH_3	16.15	16.03	0.74
Methylethyl ketone	$CH_3COC_2H_5$	20.65	20.66	0.05
Diethyl ketone	$C_2H_5COC_2H_5$	25.18	25.29	0.44
n-Butyl aldehyde	C_4H_9COH	20.64	20.66	0.10
Methyl alcohol	CH_3OH	8.22	8.24	0.24
Ethyl alcohol	C_2H_5OH	12.74	12.87	1.02
n-Propyl alcohol	C_3H_7OH	17.52	17.49	0.17
iso-Amyl alcohol	$C_5H_{11}OH$	26.74	26.73	0.04
Methylal	$CH_3OCH_2OCH_3$	19.19	19.32	0.68
Ethylpropyl ether	$C_2H_5OC_3H_7$	26.95	26.90	0.18
Ethyl ether	$C_2H_5OC_2H_5$	22.43	22.28	0.67

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[1] Swietoslawski, *J. Am. Chem. Soc.*, **42**, 1,945 (1920).

This effect[1] is 1.73 for a double bond and 2.40 for a triple bond.

Molecular refractions of dissolved salts are nearly additive at all concentrations,[2] if it is assumed that no change in the refraction of water results when a salt is dissolved in it. The increase in specific refraction due to added salt, multiplied by the molecular weight of the salt, has a value which may be divided among the separate ions in the way shown in Table 109.

TABLE 109.—MOLECULAR REFRACTIONS OF DISSOLVED SALTS AT 25°, SHOWN AS AN EFFECT FOR THE SEPARATE IONS. CHANGING IONIZATION HAS A VERY SMALL EFFECT UPON THE OBSERVED MOLECULAR REFRACTION

Ion	H	Cl	Br	I	Li	Na	K
Atomic refraction......	1.03	7.50	11.05	17.68	1.27	1.75	3.84

Boiling Points.—These generally increase from member to member of homologous series as shown in Fig. 46. It will be seen that the increase for a —CH_2— group becomes smaller for higher members of the series. This is expressed by Young's equation, from which the boiling point of a member of an homologous series may be calculated from that of the next member of the series below it. Let T be the boiling point of a compound, and T' that of the next higher member. Then

$$T' = T + \frac{144.86}{T^{0.0148T}}.$$

This expression applies not only to hydrocarbons of the straight chain type, but to their derivatives as well.

A given fractional change in pressure usually produces the same *fractional* change in the absolute boiling points of different substances, provided the change in pressure is not too large. Thus a decrease of 5 per cent in total pressure lowers the boiling point of water 1.4°, which is 0.37 per cent of its absolute boiling temperature, 373. This same decrease of pressure should lower the absolute boiling point of alcohol 0.37 per cent; the calculated lowering is 1.3°, that experimentally measured is 1.2°. In many cases the agreement is much better than this, but this fairly represents the average case. Some further illustrations are given on page 75.

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[1] Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911). His values for the other atomic refractions quoted above are R_C 2.418, R_H 1.100, R_{CH_2} 4.618, 2.211 for carbonyl oxygen, 1.643 for ethereal oxygen, 1.525 for hydroxyl oxygen, R_{Cl} 5.967, R_{Br} 8.865, R_I 13.90.

[2] Baxter, *J. Am. Chem. Soc.*, **33**, 901 (1911).

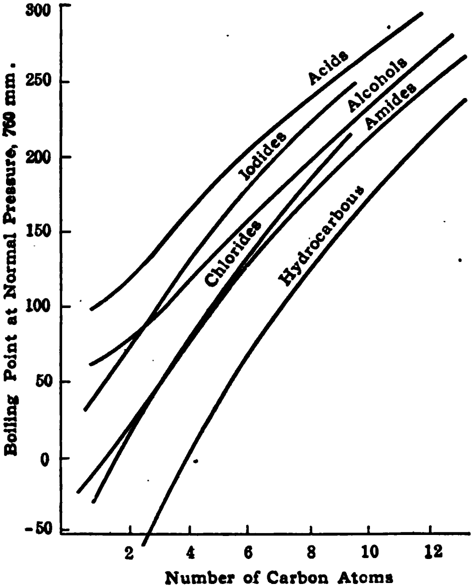

FIG. 46.—Boiling points in homologous series.

An elevation of boiling point usually results upon substitution of a higher boiling element in organic compounds; methyl chloride boils higher than methane, methyl iodide boils at a still higher temperature, and the same general effect is observed throughout a series.

Heats of Combustion.—Each higher member of an homologous series is formed from the one below it by adding a —CH_2— group; if the heat of combustion is an additive property, the difference for adjacent members in a series should be a constant, equal to the heat of combustion of one —CH_2— group. This heat of combustion has been estimated[1] at 153,500 cal. for each

[1] Richards and Davis, *J. Am. Chem. Soc.*, **42**, 1,616 (1920).

such group. The extent of variation to be expected is illustrated by the data for a series of alcohols.

TABLE 110.—HEAT OF COMBUSTION OF ALCOHOLS

Substance	Molal heat of combustion	Difference for CH_2
Methyl alcohol	170,610	
Ethyl alcohol	327,040	156,430
Propyl alcohol	485,800	158,760
Butyl alcohol	638,330	152,530
iso-Butyl alcohol	637,140	151,340

The effect of constitution is clearly shown by the difference between the quantities of heat evolved from a mol of butyl alcohol and a mol of its isomer. Other additive relations are considered briefly in connection with the bonds severed during combustion, for which see page 199.

Specific Heats.—The molecular heat capacity of a solid compound is approximately the sum of the atomic heat capacities of its elements. But as some elements which exist in solid compounds are not solids at room temperature, their atomic heat capacities in solids must be determined by experiment. Thus the difference between the atomic heat capacity of zinc and the molecular heat capacity of zinc oxide is 4 cal., and this is the effective atomic heat capacity of oxygen in solid oxides. Similar figures have been obtained for chlorine, sulfur, hydrogen and other elements in an analogous way. It should be noted that solids of low atomic heat capacity (boron, sulfur, carbon) in the uncombined state retain these lower values in compounds. The average effective atomic heats are given on page 96, together with data illustrating the additive heat capacities.

CHAPTER XII

PERIODIC LAW OF THE ELEMENTS

Mendelejeff's periodic law states that when the elements are arranged in order of increasing atomic weight, there is a recurrence of chemical properties every eighth element. In some cases a recurrence of properties came in the seventh element, from which Mendelejeff rightly concluded that in this "period" there was a missing element yet to be discovered. By writing the elements in eight columns and leaving blank spaces where they seemed to be required in order to bear out the periodic law, he obtained the familiar periodic table. Of course if an element should be discovered for which there was no blank place, an alteration in the periodic table would be made necessary. Just this thing happened in the discovery of argon, an element which did not resemble any known element; further researches brought to light a whole family of these elements, and another column was therefore made necessary in the table. The arrangement at present accepted is shown in Table 111. It contains three elements, gallium, scandium and germanium, which were unknown to the discoverer of the periodic law; but he predicted the properties which these elements should have when discovered, and his predictions were confirmed by experiment after these elements were found.

The so-called rare earths disturb the periodic table unless several of them are assigned to a single place in the table; all of them have properties corresponding to this place and it seems proper that all of them should go in the one position. Eleven elements therefore occupy the place of lanthanum. Further study is needed to reveal the reason for this crowding of a single place; but the best that can be done at present is to leave all of them in this place. Indeed, if a similarity of properties is the basis of grouping elements in the periodic system, this similarity exists in the case of the rare earths to an extent which makes their separation exceedingly tedious and difficult.

Similar cases exist among the radioactive elements, where several elements occupy a single position in the periodic table; and the properties of elements in any one position are practically identical, so that effective separation has yet to be accomplished by any means. These elements have different atomic weights, but appear to be identical otherwise, while the rare earth elements have properties (such as solubility) which differ very slightly from element to element.

There are other irregularities in the periodic arrangement of elements according to atomic weight which are difficult to understand, and for which there are no explanations at present. Iodine has a smaller atomic weight than tellurium and should therefore come in the column with sulfur, while tellurium then falls in the halogen column. It was at first thought that this indicated an error in the atomic weight determinations, but a large number of very careful experiments have shown that this is not the case. We therefore disregard the order based on atomic weight in making up the halogen column, and put iodine out of order so far as its atomic *weight* is concerned. It will be shown later that there is another property more fundamental than the weight of atoms, and that when the elements are arranged according to this property, there is no such discrepancy; iodine falls in its proper place. Another pair of elements in the table is also out of order if the weight order is followed; argon should fall in the alkali metal column and potassium in the inert gas column. Here again the elements are placed in the column required by their chemical properties and the weight order is disregarded.

Leaving out of consideration the exceptions to this periodic law, the elements may be arranged in the way shown in Table 111. Under each element in this table is a number which is its order number in the arrangement. Elements 43, 61, 75, 85 and 87 have not yet been discovered, but the grouping which corresponds to the physical and chemical properties of the elements is disturbed unless blanks are left in the table for these elements. Thus if element 43 is ruthenium and no blank is left, this member of the platinum group is shown as a homologue of manganese, but it resembles manganese in none of its properties; similarly element 75 (also a homologue of manganese) has not yet been discovered. These numbers are now quite generally called the *atomic numbers* of the elements. The exceptions to Mendelejeff's periodic law disappear when it is stated in the form: The chemical and physical properties of the elements are periodic functions of their atomic numbers.

Recently, quite definite proof that the atomic numbers are a fundamental property of the elements has been obtained from X-ray bombardment.[1] When the elements are used as targets for very short-wave X-rays, each emits a series of monochromatic radiations of characteristic frequency. These radiations come from the very nucleus of the atom, on account of the violent bombardment. When the square root of the characteristic frequency for the various elementary substances is plotted against the atomic number, a perfectly straight line is obtained, as shown in Fig. 47; but this relation is disturbed if the order of the elements is that of atomic weights, just as flaws appear in the periodic table if the arrangement is that of atomic weights.

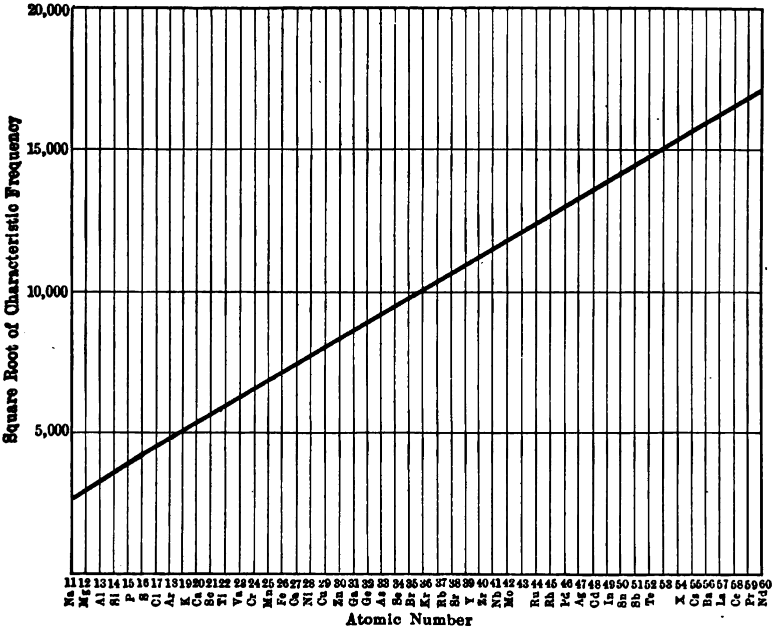

FIG. 47.—Relation of atomic number to vibration frequency.

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[1] Moseley, *Phil. Mag.*, **26**, 1,024 (1913); **27**, 703 (1914).

Other evidence justifying the arrangement which best illustrates the periodicity and which ignores some weight factors will be

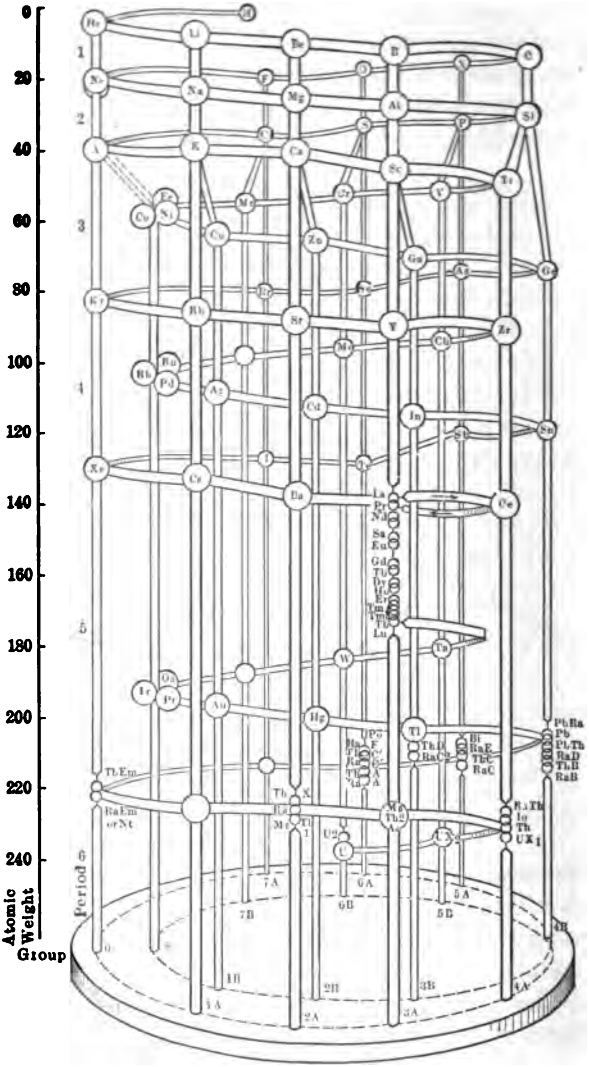

Fig. 48.—Harkins' model of the periodic arrangement of elements.

given later; though it may be said here that the atomic numbers depend upon the fundamental structure of the nucleus of the atom.

Group 0 – – – –	Group 1 R_2O – –	
He 2	H 1 Li 3	
Ne 10 A 18	Na 11 K 19	
Kr 36	Rb 37	Cu 29
Xe 54	Cs 55	Ag 47
		Au 79
Ac Em Th Em Ra Em 86	– 87	

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Moseley's experiments also afford an indication of the number of elements yet to be discovered, since the straight line showing the relation between the square root of the vibration frequency and the atomic number would exhibit displaced sections if missing elements existed, and these displacements could be eliminated by leaving a blank space for the new elements. In this way it was found that from aluminum to gold there are only three elements missing, of atomic number 43, 61 and 75, corresponding to two homologues of manganese and one rare earth.

Many arrangements of the elements in plane diagrams, on spirals, and as space diagrams have been proposed from time to time since the first periodic law was announced. Each of these arrangements brings out some particular points better than a simple arrangement in columns, but does not contribute greatly to the subject as a whole. A recent representation of the arrangement on a helix in which the atomic weight is plotted vertically[1] brings out some additional points, and is shown in Fig. 48. In it the first two "short periods," consisting of the elements helium to fluorine and neon to chlorine, form a single loop each. Following this, the longer "periods" of 18 elements each (argon to bromine and krypton to iodine) are represented by two turns each on the helix. And to allow for the rare earths, the helix makes a short special loop back from cerium (element 58) to præseodymium (element 59) which is under lanthanum (element 57); following which all of the rare earths come under this point in a vertical line, corresponding to a change of atomic weight (and increase in atomic number) with only a very slight change in chemical properties. The several elements of radioactive origin corresponding to a single position in this table also appear in vertical groups; they are connected with brackets in the simple arrangement of Table 111.

Periodic Properties of the Elements.—When the atomic volume, density, coefficient of expansion, latent heat, electrical conductivity, compressibility, melting point, boiling point, or any other physical property of the elements is plotted against the atomic number as abscissæ, a curve showing peaks and troughs periodically is obtained. Such a curve is shown for some properties in Fig. 49. If sodium occurs on a high peak, as in the atomic volume curve, potassium, cæsium and the other elements of this group also occur on peaks; these alkali elements also occur on peaks of the compressibility curve, etc. While only a few physical properties are shown in the plot, a similar curve is obtained whatever property is studied. Thus it appears that whatever internal structure of atoms is responsible for their

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[1] Harkins, *J. Am. Chem. Soc.*, **38**, 169 (1916).

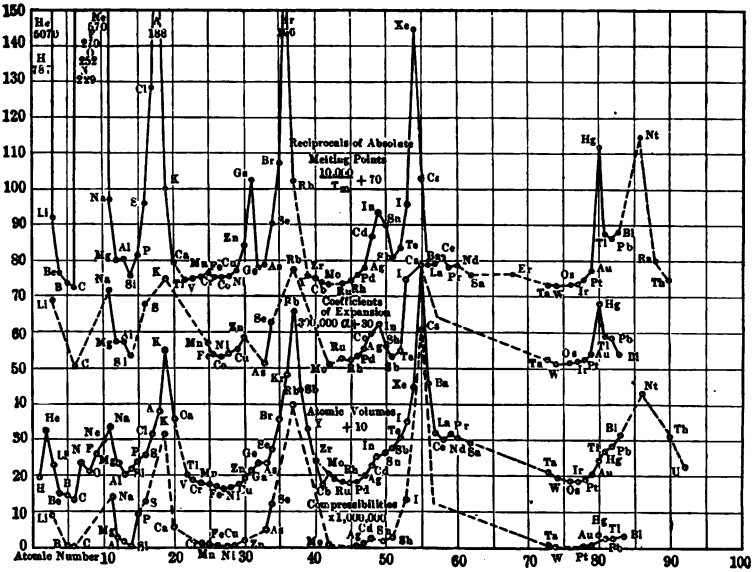

FIG. 49.—Periodic properties of the elements.

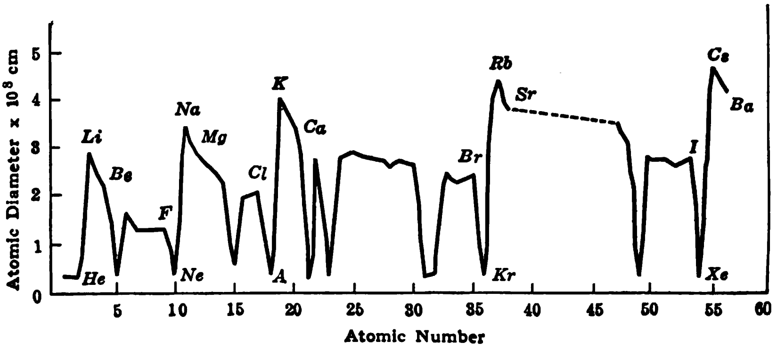

FIG. 50.—Relation of atomic number to atomic diameter.

properties, this arrangement is reproduced to a large extent after the required number of additions to the atomic mass, though it does not follow that the increments of mass are responsible for the properties. This will be explained in a later chapter.

Recent work on the distance between atomic centers in crystals has led to values for the effective atomic diameters which, when plotted against the atomic number, give a curve showing the same periodicity as that of Fig. 49. This is shown in Fig. 50.

CHAPTER XIII

RADIOCHEMISTRY

The phenomena of radiochemistry differ in many ways from other types of chemical change, but they are real chemical changes which occur at a rate corresponding to the law for a monomolecular reaction. The changes are entirely irreversible, and their rates are quite beyond control by any known means; the energy effects accompanying them are far larger than those of ordinary chemical reactions, and there is a change in the *number of atoms involved* in such reactions. These reactions proceed at the same time as the ordinary chemical reactions of the substances, and are entirely independent of them. Thus as long as an atom of radium exists as such, it is capable of combining with halogens in the same way as barium does, or it will form an insoluble sulfate; but when it undergoes its radioactive change (atomic disintegration), it yields a charged helium atom and becomes an atom of inert gas belonging to the argon family. This is therefore an atomic transmutation of one element into two others.

Alpha Particles.—Whenever a radioactive change occurs, the atom emits a charged particle of some sort. An atom of helium bearing two units of positive electricity is called an alpha particle. More properly, the alpha particle is a helium atom which has lost two electrons, or unit negative charges. These particles are expelled from atoms with a velocity of about ten thousand miles per second, and when they are directed upon a screen of zinc sulfide, a luminescence is produced. Under the microscope this is seen to be composed of separate flashes, each due to the impact of a single alpha particle. By counting the flashes in a given area, and computing the total number of particles emitted upon the assumption that the emission was the same in all directions, it has been possible to determine the total number of particles emitted per second by a quantity of radium. Other experiments have shown that these charged particles carry the same quantity of electricity as a positive bivalent ion in solution, that is, two units of positive electricity.

Beta Particles.—These are the other particles emitted during radioactive change; they consist of unit negative charges of electricity, and are not associated with matter of any kind. That is, they are "atoms" of negative electricity having no material substance, no mass. They are expelled with far greater velocity than the alpha particles.

Gamma Rays.—These also accompany radioactive changes, and they have been shown to be identical with X-rays; they are not particles, but short wave radiations like the rays produced in an ordinary X-ray tube. They result from the bombardment of the radioactive material by electrons which result from its decomposition, just as in an X-ray tube the rays result from bombardment of a target by a stream of electrons from a cathode.

Energy Effects of Radioactive Changes.—These are many times greater than those of ordinary chemical reactions. Rutherford has calculated that energy is emitted by an atomic weight of radium emanation at a rate equivalent to about 12,000 horse power,[1] and that the total energy evolved during its radioactive change to the next element in the series is equivalent to the operation of a 60,000 horse power engine for one day. This is millions of times greater than the energy of the most violent chemical reaction involving the same weight of matter, about 220 grams, or less than half a pound; but it does not mean that one possessed of the required quantity of emanation could perform this quantity of work in a day by means of it, for the emanation decomposes at its own characteristic rate and cannot be made to undergo its change in a day. The emission of energy from atomic disruptions does not controvert the law of conservation of energy, for the energy is derived from the atom itself, where it exists in kinetic or potential form. Even if some means of reversing a radioactive change were known, the amount of energy required to effect atomic synthesis cannot be less than that evolved upon atomic disintegration.

Monomolecular Reactions.—Radioactive changes are true monomolecular reactions, the velocities of which are proportional to the quantity of substance present. Thus a given very small fraction of the radium atoms present (1 in about 100,000,000,000) break up with explosive violence each second, expelling a fragment of the atom (an alpha particle) with great speed. The residual atom is lighter than before, and has become the atom of an entirely new and different element. For radium is a solid metal similar to barium, and the new atom formed is a gas belonging to the rare gas family and incapable of chemical reaction.

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[1] *Smithsonian Inst. Ann. Rept.*, **1915**, 167.

This new substance, called radium emanation, is capable of the same kind of a reaction as that which formed it; namely, an explosive disruption into another alpha particle or charged atom of helium, and a new residual substance called radium A. This latter element is very unstable, and breaks up at once, giving another alpha particle and forming a residual atom called radium B. Since in all three alpha particles of atomic weight 4 have been lost, there is a total decrease of 12 in the atomic weight from that of radium (226), and the atomic weight of radium B is therefore 214.

When radium B explodes, there is emitted an electron but no helium atom. This electron is a unit charge of negative electricity having no appreciable mass in the ordinary sense of the term, and the atomic weight of the residual atom, radium C, is therefore the same as that of its parent element, 214.

For any one of these changes the rate is strictly proportional to the number of atoms present; or in other words a fixed fraction of the total number of atoms present at any moment decompose in a unit of time. This is expressed by the law of a first order reaction (page 300),

$$\ln \frac{1}{(1 - x)} = kt.$$

However, we have here a *monatomic* reaction, since only 1 atom is involved in producing both of the reaction products. From a table of the specific reaction constants, k, for each reaction, it is possible to calculate the fraction decomposed in any interval of time. The common procedure is to compute and record the time required for half of the material to decompose, the so-called "period of half decay." Since the activity of a radium preparation (for example) depends upon the number of atoms decomposing each second, it is clear that in the half time for radium, its activity would drop to half of the original activity. When another period of this length had elapsed, the total activity is one-fourth of the original activity; one-eighth after the elapse of another such period, etc.

These changes differ from ordinary chemical reactions in that they are entirely uninfluenced by changes of temperature; a radium preparation decomposes at the same rate in liquid air as at a red heat, and regardless of the concentration or pressure. No method has yet been found of accelerating or retarding any radioactive change, that is, any atomic decomposition.

Counting Atoms.—It has already been shown (pages 63, 90, 102) that an atom is exceedingly small, and that it would be quite impossible to see a single atom or a particle containing a small number of atoms. There is, however, a means of observing the *effect* of a single charged helium atom or alpha particle, due to the great velocity (about ten thousand miles per second) with which it is discharged from radium in its decomposition. These particles are discharged in all directions, and produce a tiny flash of light when they impinge on a layer of zinc sulfide. Under a microscope it has been possible to observe the flash due to each particle. (This apparatus is called a spinthariscope.) Knowing the size of the microscope-field and its distance from the radium preparation, it is an easy matter to calculate the number of alpha particles shot out per second by the whole preparation, by means of the ratio of the area of the field to the whole spherical area which is bombarded at the same rate. The number of particles per second from a gram of radium is 1.36×10^{11}, as determined in this way.

Number of Atoms in a Gram-Atomic Weight.—Since an alpha particle which has lost its charge is in no way different from a helium atom, it follows that radium produces helium at a definite rate. Experiments have shown that the helium so produced is 0.156 c.c. per year per gram of radium. Since we have counted the number of particles shot out per second and have measured the volume of gas, we have here a means of determining the number of atoms in a gram-atom of this monatomic gas. There are 3.15×10^7 seconds in a year, therefore there are $1.36 \times 10^{11} \times 3.15 \times 10^7$, or 4.29×10^{18} alpha particles expelled per gram of radium per year, and this is the number of molecules in 0.156 c.c., whence it follows that there are 2.75×10^{19} molecules per cubic centimeter, or 6.16×10^{23} per molecular volume.[1] There could hardly be a more convincing proof of the atomic structure of matter or of the number of atoms forming a given weight of helium, for the number of separate constituents has been counted and the volume has been measured. The value so obtained is in good agreement with other determinations of Avogadro's number, based upon quite different methods. It is remarkable that radioactivity measurements which have shown that the atoms of some elements are unstable should also furnish the most convincing proof of the atomic structure of matter and of the actual reality of atoms.

Radioactive Series.—It has been established after much careful work that the familiar activity of radium is but one step in a long series of atomic transformations, some of which occur with exceedingly great velocity, others of which occupy thousands of years. The atomic changes always consist in the expulsion from the atom of alpha particles (charged helium atoms) or beta particles (negative electrons), whether they are taking place rapidly or slowly. In the following table, one such series is given in detail. Uranium, the first element in this long series of elements, changes so slowly that 5×10^9 years are required for half of it to decompose; the change consists in expelling an alpha particle, and the resultant atom is therefore lighter in atomic weight by four units. Reference to Table 112 shows that the new element, uranium X_1, is quite unstable, half of it decomposing in about 3 weeks. Since an atomic weight of uranium forms half an atomic weight of uranium X_1 in 5×10^9 years, and half of the amount present at any time decomposes in 3 weeks, it will be seen that uranium X_1 cannot be a familiar substance, and that its properties cannot be tested by ordinary chemical means, since only an exceedingly small quantity of it could be collected from any reasonable quantity of uranium.

The product of decomposition of uranium X_1 is uranium X_2, which is formed without loss of weight, since a beta particle is evolved; this element changes rapidly to uranium 2, a more stable element. At this point there is a branching in the chain of elements; only 92 per cent of uranium 2 follows the series as

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[1] Rutherford, *Ann. Rept. Smithsonian Inst.*, **1915**, 181.

TABLE 112.—RADIOACTIVE CHANGES IN THE URANIUM SERIES[1]

Element	Atomic weight	Chemical properties	Periodic group	Atomic number	Character of particle expelled	Half time value
Uranium 1	238	uranium	VI a	92	α	5 × 10^9 years
Uranium X_1	(234)	as thorium	IV a	90	β	24.6 days
Uranium X_2	(234)	(brevium)	V a	91	β	1.15 min.
Uranium 2	(234)	as uranium	VI a	92	α	10^6 years
Ionium	(230)	as thorium	IV a	90	α	10^6 years
Radium	226	like barium	II a	88	α	2,000 years
Emanation	222	none	0	86	α	2.85 days
Radium A	218	as polonium	VI b	84	α	3 min.
Radium B	(214)	as lead	IV b	82	β	26.7 min.
Radium C_1	(214)	as bismuth	V b	83	β	19.5 min.
Radium C′	(214)	as polonium	(VI b)	(84)	α	10^{-6} sec.?
Radium D	(210)	as lead	IV b	82	β	16 years
Radium E	(210)	as bismuth	V b	83	β	5 days
Radium F	(210)	polonium	VI b	84	α	136 days
Radium G	(206)	lead	IV b	82		

shown in the table. We have omitted consideration of the side series, which resembles the main one in general character, though it leads to the formation of different elements. It can be seen from study of Table 112 that the loss of an alpha particle always results in forming an atom lighter by four units than its parent, while the loss of a beta particle takes place without change in atomic mass. Those elements whose atomic weights are inferred from the character of radioactive change have been indicated in the table by enclosing the atomic weight in parenthesis. Weights not in parenthesis have been determined by the usual methods, as described in the first chapter of the book. The elements resulting from radioactive change have not, for the most part, been collected in sufficient quantities for direct chemical experiments; special methods of exceeding delicacy have been applied to determining their properties. Radium emanation has been obtained in small quantities sufficient to determine its density, and to prove that it is chemically inactive like the rare gases of the atmosphere. Some of the chemical properties of the other elements are inferred from their positions in the periodic table.

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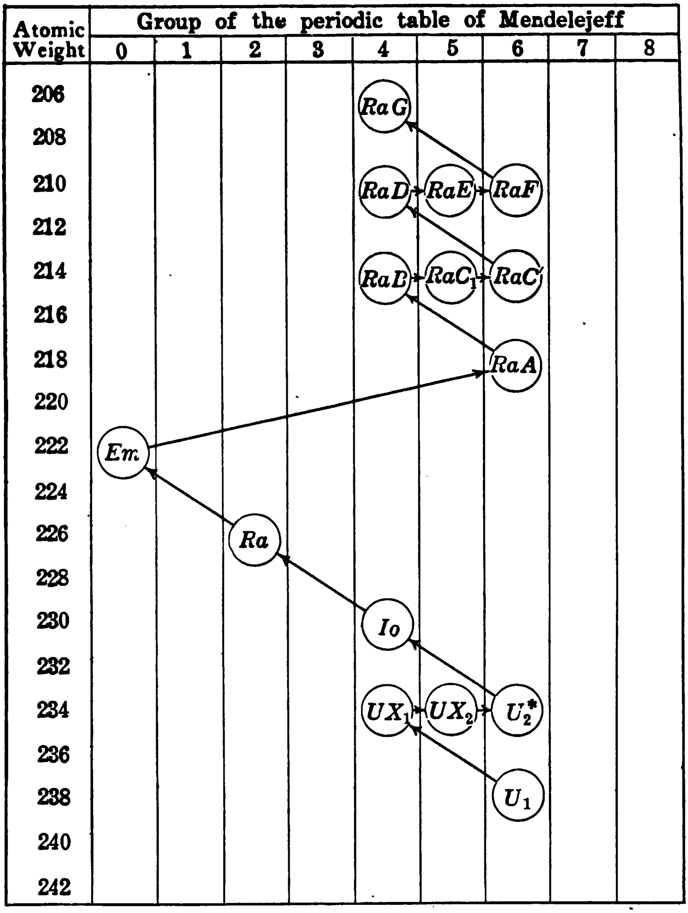
[1] Fajans, *Sci. Amer. Supplement*, **81,** 83 (1916). Other writers give slightly different values for the period of average life. Compare Soddy's text book, or Rutherford, *Smithsonian Inst. Report*, **1915,** page 185.

Radioactivity and the Periodic Table.—As may be seen from Table 113, the loss of an alpha particle shifts the position[1] of an element in the periodic table two places to the left, and the loss

TABLE 113.—RADIOACTIVE CHANGES IN THE URANIUM SERIES, IN RELATION TO THE PERIODIC TABLE OF THE ELEMENTS



* At uranium 2 there is a branching in the chain of radioactive changes, and only 92 per cent of uranium 2 follows the changes here shown; the remainder undergoes a different set of decompositions of the same general character as those of the main series.

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[1] Soddy, *Nature*, **102**, 356 (1919).

of a beta particle moves it one column to the right. Thus, the loss of one alpha particle and two beta particles brings an element into the column from which it started, but with a decrease of four units in atomic mass. It should therefore have properties similar to those of the parent element after such a change, and this is found to be the case. So far as their properties have been studied, there appears to be no chemical difference whatever between radium B, radium D and radium G (supposed to be the stable element lead), though the atomic weights change by four units. Here we have definite proof that atomic mass is not the determining factor in chemical properties. In considering the periodic table in general, it was found necessary to follow the order of *atomic numbers* in arranging elements; the question arises, will this settle the present difficulty? It will; but the settlement is a little surprising, for these elements radium B, radium D and radium G have the *same* atomic number, and therefore occupy the *same* place in the periodic table. Since they behave chemically in exactly the same way (that is, as the same element), and occupy the same place in the periodic table, why not call them all the same element? This might be done if the atomic weights were not different by four units. Can an atom yield an atom of helium upon disintegration, and then by the loss of two electric charges become again the same element? If its atomic weight is a fundamental property of an element, no; if chemical identity in every other way constitutes the governing factor, yes.

Isotopes.—Isotopic elements are identical in every way except atomic mass. That is, the elements radium B, radium D and radium G are isotopes of lead; they have the same atomic number as lead, occupy the same place in the periodic table, are identical with it in chemical properties, and inseparable from it; but they are of different atomic mass. A specimen of lead in which some radioactive change is still going on would presumably contain some of radium D or radium B. As seen from the table, the atomic weight of radium G should be 206, since it is formed from radium (atomic weight 226) after the loss of five alpha particles, each of atomic weight four. The experimental value for the atomic weight of ordinary lead is 207.20, but as it is not in the least radioactive, it cannot be a mixture of these isotopes. The inactive end-element of another disintegration series known as the thorium series is also an isotope of lead, with an atomic weight 208.1, and it might be possible that ordinary inactive lead is a mixture of these two inactive end-products.

Several questions will occur at once. Can inactive lead ever be found with an atomic weight other than 207.2, due to mixture of inactive isotopes in different proportions? Can a substance chemically identical with lead, but of different atomic weight, be prepared from the lead of radioactive minerals? Can this radioactive lead be separated into two components, one of which is inactive lead of atomic weight 207.2? Can ordinary lead be separated into two components of atomic weight 206.0 and 208.1? The first and last of these questions may be considered together. Specimens of lead minerals from various parts of the world were collected,[1] and the lead in them was subjected to most careful purification by several different chemical processes. The atomic weights were found to be identical, and all of the specimens were found to be inactive lead. These results are shown in Table 114. If lead was separable into fractions of different atomic weights, this would have been brought out by the different methods of purification, some of which would eliminate one constituent more completely than the others. If the two isotopes occur mixed in different proportions, this should be brought out upon examining specimens from widely separated sources. Neither of these expectations was realized, and so far there is therefore no evidence that ordinary lead is a mixture.

TABLE 114.—ATOMIC WEIGHT OF INACTIVE LEAD FROM VARIOUS SOURCES

Source of lead	Atomic weight	Source of lead	Atomic weight
Commercial lead salt....	207.22	Cerrusite from Australia	207.22
Eifel Mts., Germany....	207.20	Galena from Missouri...	207.22
Cerrusite from Idaho....	207.21	Galena from Germany..	207.21
Vanadinite, Arizona....	207.21	Galena, Washington....	207.21

"Lead" from radioactive minerals collected at widely separated points[2] has an atomic weight which is far from that of ordinary lead, and different in different minerals. The methods of purification were as carefully selected as in the case of ordinary lead above. Careful spectrum analysis showed the absence of impurities in the specimens of lead, and experimental errors large enough to account for this difference are entirely out of the question, as the work was done with extreme care by experienced workers. Finally,[1] a large quantity of radioactive lead (atomic weight 206.41) was converted into nitrate, and this was subjected to a series of fractional crystallizations (such as are used to separate the rare earth elements) until about a thousand fractionations had been performed. The most soluble and least soluble end-portions showed no difference of atomic weight, and no difference in beta-ray activity; hence this number of crystallizations effected no separation.

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[1] Baxter and Grover, *J. Am. Chem. Soc.*, **37**, 1,027 (1915).

[2] Richards and Lembert, *J. Am. Chem. Soc.* **36**, 1,329 (1914); **38**, 2,613 (1916).

TABLE 115.—ATOMIC WEIGHT OF RADIOACTIVE "LEAD"

Source of lead	Atomic weight
Norway clevite	206.08
North Carolina uraninite	206.40
Australian carnotite	206.38
Joachimsthal pitchblende	206.57
Colorado carnotite	206.59
Ceylon thorianite	206.82
English pitchblende	206.86
Colorado carnotite	207.00

The isotopes of lead have identical atomic volumes,[2] hence different densities; that of ordinary lead is 11.337 and that of radioactive lead 11.289 in one specimen and 11.273 in another (atomic weight 206.08). The molal solubilities are identical[3] for the nitrates of isotopes; their indices of refraction and their spectra are also identical.[4] No method of separating them has yet been found effective for lead, and we are therefore forced to conclude that elements which have different atomic weights may have identical chemical properties, such that the isotopic forms are absolutely inseparable; and that elements of different atomic weight must be assigned the same place in the periodic table.

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[1] Richards and Hall, *J. Am. Chem. Soc.*, **39**, 531 (1917).

[2] Richards and Wadsworth, *J. Am. Chem. Soc.*, **38**, 1,658 (1916).

[3] Richards and Schumb, *J. Am. Chem. Soc.*, **40**, 1,409 (1918).

[4] Merton, *Proc. Roy. Soc. London*, **A96**, 388 (1920) and Harkins, *J. Am. Chem. Soc.*, **42**, 1,329 (1920) claim to have found very slight differences in the spectra of isotopic forms of other elements.

Isotopes of Light Elements.[1]—Evidence of another sort has been obtained that many elements are isotopic, that is, contain *chemically identical* atoms of different weight. When the positive rays from a discharge tube are passed between charged plates, they are deflected toward the negative plate. By means of apparatus arranged as in Fig. 51, positive rays are sorted into an extremely thin ribbon on passing through the parallel slits S_1 and S_2, and are then spread into an electric spectrum by means of the charged plates P_1 and P_2, of which the latter is negative. A portion of this spectrum deflected through a given angle is selected by the diaphragm D and passed between the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through a greater angle than that of the first deflection. The result of this is that rays having a constant mass (or more properly a constant ratio m/e of mass to charge) will converge to a focus at F and indicate their position upon a photographic plate placed as shown, giving a spectrum dependent upon mass alone. On account of its analogy to optical apparatus, the instrument is called a positive ray spectrometer and the spectrum produced is known as a mass spectrum. A sketch of the spectrum obtained for neon is shown in Fig. 52. Displacement to the right with increasing mass is

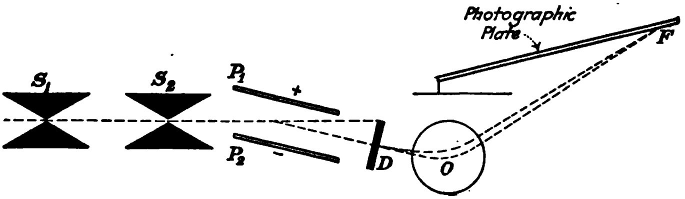

FIG. 51.—Positive ray spectrograph.

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[1] Aston, *Nature*, **104**, 393 (1919); **105**, 617 (1920); *Phil. Mag.*, **39**, 449 (1920); *Science Progress*, **15**, 212 (1921).

seen to be approximately linear, the numbers indicate masses corresponding to O = 16. Only relative measurements are obtained, in terms of particles of known mass. These particles are impurities in the gas investigated, sometimes introduced purposely to aid in the smooth operation of a discharge tube. The principal groups of reference spots shown correspond to oxygen 16, two lighter spots at 24 and 26 are probably C_2 and C_2H_2, and the strong spot at 28 is C_2H_4 or CO. The two chief spots for neon are shown by careful comparative measurements on the actual photographic plates to be at 20.00 and 22.00, and not at 20.2, which is the accepted atomic weight of neon. Neon therefore consists of a mixture of these two kinds of atoms, in the proportions of about nine to one.

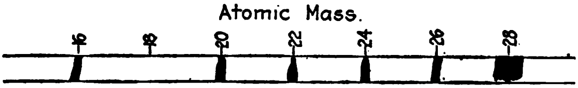

FIG. 52.—Mass spectrum of neon.

In the same way magnesium, atomic weight 24.32, has been resolved in the positive ray apparatus[1] into isotopes of atomic mass 24.0, 25.0 and 26.0. Other elements have also been resolved into isotopes, of which mercury contains perhaps 6. All of the isotopes so far encountered have atomic masses which are strictly whole numbers. A still more striking spectrum is that derived from chlorine, shown in Fig. 53.

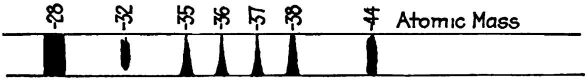

FIG. 53.—Mass spectrum of chlorine.

The strong spots at 28 and 44 are carbon monoxide and carbon dioxide, and a spot at 32 shows that a slight trace of oxygen is present. The spectrum of chlorine is characterized by four strong lines at 35.0, 36.0, 37.0 and 38.0; there is no trace of a line at 35.46, the accepted atomic weight of chlorine. The lines at 35.0 and 37.0 are due to chlorine atoms, the other lines one unit higher are their corresponding HCl compounds. This is strong evidence that chlorine consists of two isotopes whose atomic weights are whole numbers on the oxygen scale. Of course these two chlorines are chemically identical in every way, and inseparable by chemical means, so that the practical chemistry of chlorine is not disturbed in any way. Since these atoms have different atomic weights, there may be three kinds of chlorine molecules of molecular weight 70, 71 and 72. Denoting the 35 chlorine by its usual symbol Cl and the 37 chlorine by Cl′, the possible molecules are Cl_2, Cl_2' and Cl.Cl′. Molecules of different mass diffuse at different rates (Graham's law of diffusion, page 48), and it is possible that a sufficiently large number of fractional diffusion experiments may yield two samples of chlorine gas of different densities.

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[1] Dempster, *Science*, **52**, 559 (1920).

It has recently been claimed[1] that chlorine was thus separated into two portions of different atomic weight, but as no details of the separation have yet been made available, it is impossible to say to what extent the separation was carried. Even if such a separation was carried to nearly pure isotopes of atomic weight 35.0 and 37.0, the practical effect upon the law of definite proportions would be slight. There would then exist an interesting exception to this general law of universal experience which had been effected after much labor, but no important objection to the law of definite proportions. A proper discussion of this point must wait for details of the experimental procedure upon which a separation of isotopes rests.

Isotopes and the Law of Definite Proportions.—From the experiments upon the atomic weight of radioactive lead and ordinary lead, quoted above, it is clear that lead bromide contains a variable proportion of lead, according to whether ordinary or radioactive lead is concerned. These determinations of atomic weight were made from the percentage of bromine in lead bromide, as determined by precipitation of silver bromide. When isotopes are concerned, the composition of a chemical compound is a variable quantity. If it should happen that chlorine can be largely separated into fractions of different atomic weight, then chlorides may have variable compositions, according to which isotope is combined in the compound. The experiments of Aston with his positive ray spectrometer indicate that other common elements are mixtures of isotopes.

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[1] Harkins, *J. Am. Chem. Soc.*, **42**, 1,996 (1920).

This is not as serious as might at first appear. The positive ray spectrometer has not yielded weighable quantities of the separate isotopes of chlorine, and enough work has been done upon their separation in quantity to show that it can be accomplished only with very great difficulty, and after long series of fractional diffusion experiments, or other laborious methods. Isotopes have *identical* chemical properties, they are absolutely inseparable by chemical means. The quantity of radioactive lead at present available is quite small, and the practical chemistry of lead is in no way affected. So far as practical everyday chemistry is concerned, the law of definite proportions is essentially unshaken, though in stating it, a sort of mental reservation must be made for the compounds of radio-lead. No reservations are yet needed for chlorine compounds; for while the positive ray spectrometer shows convincingly that chlorine consists of two isotopes, no case is known in which these isotopes have been found separated in nature. Much careful work on its atomic weight has led to results which show that chlorine as ordinarily encountered, from whatever source, or in whatever state of combination, behaves as an element of atomic weight 35.46; long experience has shown that it may be considered as an elementary substance. There is not the slightest probability that chlorine will be separated into its isotopes in sufficient quantity to influence its everyday chemistry, so long as this separation looks to fractional diffusion methods or to positive ray separation.

Age of Minerals.—If all of the lead in a mineral is of radioactive origin, and all of it has come from decay of uranium, then a calculation of the age of the mineral may be made from the known rate of decay of uranium. This calculation has often been made, and the results agree as to the order of magnitude, but it is quite uncertain that all lead in any mineral was so formed, and that no other alteration has taken place in a mineral in the enormous time interval involved. Most of such calculations lead to the order 10^9 years,[1] but the individual calculations of various authorities vary between 1×10^9 and 11×10^9.

Thorium Series.—In addition to the uranium series of radioactive changes already discussed, there is another series of which thorium is the parent element. The changes involved consist of the expulsion of alpha and beta particles, with corresponding losses in atomic weight when the former are lost, and with the corresponding shifts in position of the elements in the periodic table. The end product of this series is isotopic with ordinary lead, just as is the end product of the uranium series; it is formed from thorium (atomic weight 232.1) with the loss of 6 helium atoms, and should therefore have an atomic weight 24 units less than thorium, or 208.1. It will be noted that this is higher than the atomic weight of ordinary lead, while the end product in the uranium series has an atomic weight lower than ordinary lead. It is possible that ordinary lead is a mixture of these two inactive end products, always in constant proportion, but this is exceedingly unlikely in view of the work on the atomic weight of inactive lead from widely separated sources mentioned above. In all of the specimens of inactive lead there examined, none had an atomic weight deviating by more than 0.01 unit from the average. Perhaps there are three leads, an inactive one (ordinary lead) and the two active end products.[1] At least a specimen of lead thought to have come from thorium disintegration has shown an atomic weight of 207.90, which is higher than that of ordinary lead,[2] but which cannot be the pure end product, since this should have the atomic weight 208.1.

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[1] See F. W. Clarke, *Proc. Nat. Acad. Sci.*, 4, 181 (1918).

Actinium Series.—This third series contains no elements of long life, and has the same general characteristics as the others already described. It need not be given in detail here.

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[1] Clarke, *Proc. Nat. Acad. Sci.*, **4**, 181 (1918).

[2] Hönigschmid, *Physikalische Ztsch.*, **19**, 436 (1918)

CHAPTER XIV

ATOMIC STRUCTURE

We have seen in earlier chapters that the distance between atomic centers in liquids and solids is of the order 10^{-8} centimeters, or about a thousandth of the shortest wave length of visible light. It is therefore clear that any evidence of the internal structure of such a particle is necessarily indirect. Indeed, it seems almost impossible that anything at all could be known of such an exceedingly tiny particle. Not many years ago, mention of the chemical analysis of stars and planets would have seemed as far removed from possibility; yet this has been accomplished through their spectra, and one element (helium) was shown to be present in the sun before it was discovered on the earth. The elucidation of atomic structure is not more remarkable.

Evidence Already Presented.—From consideration of the periodic table it seems probable that something within the atom which is responsible for many of its chemical properties is repeated every eighth element. In attempting to visualize its structure, it is therefore necessary to have a similar arrangement within the atom every eighth element when they are arranged in the order of increasing atomic numbers. We have seen from the phenomena of radioactivity that helium atoms are expelled from heavy metal atoms during atomic disintegration of one type, and that negative charges are expelled in another type of radioactive change; hence these must form the fundamental constituents of these atoms, and presumably of the more stable atoms as well. There are eight radioactive transformations in which helium atoms are expelled in the uranium series, six in the thorium series and five in the actinium series. The probability that helium is one of the units of atomic structure in other atomic structures as well as those involved in radioactivity is strengthened by the fact that the atomic weights of a number of elements differ by exactly four units.

The fact that the helium nucleus survives the violent expulsion from a radioactive atom suggests that it is a very stable unit. A substance which breaks up with the emission of swiftly moving electrons (beta particles) follows the same laws as one which gives out helium atoms. It is therefore probable that these electrons also come from the same part of the exploding atom, and that they are constituents of the complex atom in the same way that the helium atoms are. The atoms of elements are not electrically charged when in the free state, hence there must be an equal number of positive and negative charges in them.

Two simple possibilities present themselves. Either all of the positive electricity is on the outside of the atom and the negative electricity within it; or the positive electricity is concentrated in the interior of the atom and the negative electric charges are on the outside. It is certain that positive electricity is to be found associated with the mass of the atom in either case, for positive electric charges having no appreciable mass have never been observed. Electrons (negative charges) do exist without association with matter of any kind; they are in effect mass-less "atoms" of electricity; no corresponding positive electorn is known.

Scattering of Alpha Particles by Matter.—When a beam of swiftly moving alpha particles is passed through gold, an occasional particle is deflected through an angle greater than a right angle, presumably on account of having entered into the very core of an atom and there encountered an intense electric field. In order to account for the intensity of this field it is necessary to suppose that the positive electricity is concentrated in a very minute volume (compared to the distance between atoms), or nucleus. The field which could come from a uniform distribution of the positive electricity around a sphere 10^{-8} centimeters in diameter is far from strong enough to explain the observed deflections of alpha particles.

Rutherford Atom Model.—It is now commonly accepted that an atom consists of a small positive nucleus with which is associated the mass of the atom, and a system of electrons which form the outer layer of it. The material in the following pages relates first to the structure and diameter of this inner mass nucleus; second to the number and arrangement of the outer electrons, and the relation of this arrangement to chemical behavior. Evidence bearing on both topics is of necessity indirect or circumstantial; much of it is mere plausible speculation, but it is worthy of attention and study, for it points the way to future research and serves as a working basis in present problems. A nuclear structure was first proposed by Rutherford,[1] and such a model is often called after him.

Atomic Number.—In the previous chapter it was stated that when the elements were arranged in the order of increasing atomic weight (after such irregularities as the positions of argon and potassium, tellurium and iodine, etc., were eliminated by placing these elements in their proper columns), the order number of each element was called its atomic number. Except for the evidence based on vibration frequency, there was nothing to indicate that the atomic number was anything more than the order number, arbitrarily changed in two or three cases to make the periodic table more systematic. If we define the atomic number of an element as the *number of positive charges on its nucleus,* as determined in experiments on atomic structure, the same order is obtained as in the periodic system. In fact, there is a simple relation between atomic number and the frequency of characteristic X-ray spectra, as determined by Moseley's experiments mentioned in the previous chapter. If n is the atomic number as defined above (magnitude of the positive charge on the nucleus of an atom), and f is the frequency of vibration,

$$f = a(n - b)^2,$$

where a and b are constants. The elements when arranged according to the atomic numbers thus determined, fall into their proper places in the periodic table. Hence the atomic number of an element is a more fundamental property of it than its weight. *The atomic number of an element is the number of positive charges on its nucleus.* These atomic numbers are also deduced from scattering of X-rays on passing through matter, and from the scattering of alpha particles; the same number being obtained by any of the methods.

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[1] *Phil. Mag.*, **21**, 669 (1911); **26**, 702 (1913); **27**, 488 (1914).

Structure of Atomic Nuclei.[1]—From the closeness of the low atomic weights to whole numbers if oxygen is 16.000, and from the relative abundance in the earth's crust of elements of even atomic number, a theory has been postulated as to the origin of elementary atoms,[2] which assumes their nuclei to be built up from alpha particles (positively charged helium atoms), positively charged hydrogen atoms, and electrons; the latter not contributing to the mass of an atom to an appreciable extent. Those elements whose atomic weights are divisible by four (carbon, oxygen, neon, magnesium, silicon, sulfur, etc.) are considered as built up of a nucleus containing the required number of helium nuclei to give the proper weight; thus $3He^{++}$ for carbon, $4He^{++}$ for oxygen, $5He^{++}$ for neon, etc., plus a system of electrons in a shell surrounding the atom, such that the atom as a whole is electrically neutral. On account of the great stability of helium, these atoms of even atomic number, which are supposed to contain helium only, should be more stable than those of odd atomic number, which are supposed to contain hydrogen in their structure. There is no direct test of the stability of any of the nonradioactive elements, since they are unchangeable by all physical and chemical means within our power, but if they were really built up in the way here postulated, the more stable ones should be more abundant in the universe. Meteorites contain about 99 per cent of elements of even atomic number; the earth's crust contains about 90 per cent of these elements.

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[1] The student of chemical history will recognize in the considerations of this paragraph a modification of Prout's hypothesis (1834) that the atomic weights were exact multiples of that of hydrogen. The underlying thought of this hypothesis is a building up of elements from hydrogen as a fundamental constituent of all matter. Clarke (1873) long ago postulated an evolution of elements, and this has been supported in late years by spectroscopic observation of the planets. Lockyear and others have pointed out that the spectra of hydrogen and helium predominate in the hot stars. Evolution of elements is indicated by a progressive increase in chemical complexity of the heavenly bodies as their temperatures decrease from those of the simple gaseous nebulæ to the sun and colder planets like the earth. The more complex (heavier) elements do not appear until lower temperatures are reached. The spectrum lines of lead appear in the solar spectrum, while those of uranium and thorium do not appear. Against this plausible argument must be set the facts of radioactivity; namely, that uranium and thorium do break up their atoms spontaneously, with the formation of an end product chemically identical with lead. Here we are able to observe an uncontrolled and spontaneous disintegration of atoms; no synthesis of atoms of any kind has been observed, though the spectra of stars indicate the possibility that it does take place at exceedingly high temperatures. See Clarke, *Proc. Nat. Acad. Sci.*, **4**, 181 (1918).

[2] Harkins, *Science*, **50**, 577 (1919); *Nature*, **105**, 230 (1920); *Physical Review*, **15**, 73 (1920); *J. Am. Chem. Soc.*, **39**, 856 (1917); **42**, 1956 (1920).

Direct proof of this bold hypothesis has not been accomplished, but the evidence in its favor commands attention. All of the atomic weights of the lighter elements are what this hypothesis would require, provided there is a decrease of 0.76 per cent in mass due to the "packing effect" of the component nuclei. The ~~elements consisting~~ of helium only are much more abundant. Heavy elements do actually give off helium during their radioactive changes. Finally,[1] hydrogen seems to have been obtained as a result of extremely violent bombardment of nitrogen molecules with alpha particles (charged helium atoms) of exceedingly high velocity, while no hydrogen was obtained from similar bombardment of oxygen molecules. Harkins' hypothesis states that nitrogen contains hydrogen nuclei and that oxygen contains none, and this remarkable experiment by Rutherford thus seems to be a confirmation of Harkins' views. However, Rutherford himself expresses some reserve in making a statement that atomic transmutation has been effected, and is inclined to experiment further. On the basis of the present evidence, his interpretation seems unavoidable, and in harmony with Harkins' postulate of atomic origin.

Following this line of speculation further, a new periodic table (Table 116) has been prepared which shows the structure of each atomic kernel and the agreement between the atomic weight calculated on the assumption of such a nuclear structure with that based on the usual methods of determining atomic weights. This system of representing atomic structure falls down after the third period of the table, and atomic weights which are not close to whole numbers are more common from this point on. In the first 28 elements there are cases in which the atomic weights are not close to those demanded by this hypothesis. In some of these cases it has been shown by other investigators[2]

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[1] Rutherford, *Phil. Mag.*, **37**, 571 (1919); *Science* **50**, 467 (1919).

[2] Aston, *Nature*, **104**, 393 (1919); Dempster, *Science*, **52**, 559 (1920).

TABLE 116.—HYDROGEN-HELIUM STRUCTURE OF ATOMS (According to HARKINS)

	Even group 0	Odd group 1	Even group 2	Odd group 3	Even group 4	Odd group 5	Even group 6	Odd group 7
Atomic number	2	3	4	5	6	7	8	9
Element	He	Li	Be	B	C	N	O	F
Atomic structure	He	He + H_3	2He + H	2He + H_3	3He	3He + H_3	4He	4He + H_3
Calculated atomic weight	4.0	7.00	9.00	11.0	12.0	14.00	16.00	19.00
Determined atomic weight	4.0	6.94	9.10	10.9	12.0	14.01	16.00	19.0
Atomic number	10	11	12	13	14	15	16	17
Element	Ne	Na	Mg	Al	Si	P	S	Cl
Atomic structure	5He	5He + H_3	6He	6He + H_3	7He	7He + H_3	8He	8He + H_3
Calculated atomic weight	20.0	23.00	24.00	27.0	28.0	31.00	32.00	35.00
Determined atomic weight	20.2	23.00	24.32	27.1	28.3	31.04	32.06	35.46
Atomic number	18	19	20	21	22	23	24	25
Element	A	K	Ca	Sc	Ti	V	Cr	Mn
Atomic structure	10He	9He + H_3	10He	11He	12He	12He + H_3	13He	13He + H_3
Calculated atomic weight	40.0	39.00	40.00	44.0	48.0	51.00	52.00	55.00
Determined atomic weight	39.9	39.10	40.07	45.1	48.1	51.0	52.0	54.93

from the deflection of charged atoms or positive rays in a powerful electric field that the element consists of two isotopes of different atomic weight. Thus neon consists of 9 parts of an atom with atomic weight 20.00 and 1 part of atomic weight 22.00, which is in agreement with the value 20.2 in the international table of atomic weights. Chlorine contains 2 isotopic atoms of weight 35.0 and 37.0 respectively; from the mass spectrum of these atoms (of course mixed in the proportion to give an apparent atomic weight of 35.46) it was found that there are no other isotopes present in chlorine.

Finally,[1] Harkins claims to have separated chlorine by a series of diffusion experiments into its two components. No element which has thus far been examined by the deflection of its positive rays has an atomic weight which is other than a whole number except when isotopes have been indicated by two kinds of positive rays.

In connection with this table, it should be noted that the increment in weight between the first series of elements (helium to fluorine) and the second series (neon to chlorine) is 16, or 4 He, the increment from this series to the following one is 5 He, and the increment to the next series, not shown in the table, is 6 He. This increment persists even in the elements of odd atomic weight, such as lithium, boron and fluorine. There is an unexplained exception in the increase in weight from nitrogen to phosphorus, which is 17 in place of 16, and other exceptions occur with increasing frequency for elements of higher atomic weight. This indicates that there is some other law yet to be discovered which regulates these increases. If the actual atomic weights of the elements supposed to consist of helium nuclei only are divided by the number of such nuclei present,[2] values for the atomic weight of helium are obtained as shown in Table 117.

The author of this hypothesis of atomic structure considers that he has good reason for omitting from consideration the elements in Table 117 which are enclosed in parenthesis. The strength of his theory is much weakened by the fact that he does not find any reason for omitting an element whose atomic weight is an exact multiple of four, but does discard magnesium and silicon. However, there can be little doubt that some truth underlies these speculations; radioactive changes show that helium is beyond question a constituent of the heavier atoms, and it would be strange if it were not in the nucleus of lighter atoms as well.

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[1] *J. Am. Chem. Soc.*, **42**, 1,996 (1920).

[2] Harkins, *J. Am. Chem. Soc.*, **42**, 1,988 (1920).

TABLE 117

Element	Number of helium nuclei	Atomic weight of helium	Element	Number of helium nuclei	Atomic weight of helium
Carbon	3	4.001	Titanium	12	4.008
Oxygen	4	4.000	Chromium	13	4.000
(Neon)	5	(4.040)	Iron	14	3.989
(Magnesium)	6	(4.050)	Thorium	58	4.003
(Silicon)	7	(4.045)	Uranium	59	4.003
Sulfur	8	4.008	Radium	56	3.998
Argon	10	3.990	Radio-lead	51	4.001
Calcium	10	4.007			

Number and Arrangement of Electrons in Atoms.—If the atomic number is the number of positive charges on an atomic nucleus, it is also the number of electrons entering into an atomic structure, since atoms as a whole are electrically neutral. These electrons are sometimes assumed to rotate around the atom[1,2,3] in such a way as to give rise to the characteristic spectra, but for elements containing several electrons, it will be seen that such a system of rotations would be very complicated. A more important objection to this idea is that it does not bring about a repetition of any arrangement every eighth element, as it should to account for the periodic table. Many have discarded this idea in favor of an assumption that the electrons around an atomic nucleus are more or less stationary, and vibrate only within a range which is narrow compared to the atomic diameter. Since the recurrence of properties comes every eighth element, it is natural to assume that the electrons occupy nearly stationary positions at the corners of an imaginary cube circumscribed

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[1] Bohr, *Phil. Mag.*, **26**, 1, 477, 857 (1913); **30**, 394 (1915).

[2] Nicholson, *Phil. Mag.*, **27**, 541 (1914); **28**, 90 (1914).

[3] Kossel, *Ber. deut. physik. Ges.*, **16**, 953 (1914).

about the atomic nucleus.[1] The existence of isotopic elements having identical chemical properties and different atomic weights (therefore different nuclear structures as well) clearly shows that the nucleus does not determine the chemical properties of elements. It is natural to seek the explanation in the arrangement of electrons, for that reason. Let us consider a few simple elements in detail.

Hydrogen and Helium.—A hydrogen atom has but one electron, helium has two which are supposed to be situated on opposite sides of the atomic nucleus. This arrangement of electrons is probably the most stable of any, and helium is probably the most stable element. Two hydrogen atoms combine to form a molecule, their electrons forming a stable pair. These elements are not considered in the cubical arrangement, which begins with lithium.

Lithium to Neon.—Lithium has three electrons and three positive charges upon its nucleus. Two electrons are assumed to be within the cube, forming a pair such as that in a helium atom or a hydrogen molecule, but this pair is not shown in drawing the diagrams. This is also the case in all of the following elements. The third electron in lithium, the third and fourth in berylium, etc., have the positions shown[2] in Fig. 54.

It is assumed that every element having an incomplete set of eight electrons, an "octet" of electrons around it, tends to complete this octet if it is nearly full already; or to give up its electrons to complete the octet of another element in case it has few of them. Thus lithium has no tendency to take on seven other electrons to complete its octet, but readily gives up its one electron to complete the octet of fluorine. Neon, having a complete octet of its own, neither gives up electrons to any other element or takes on any from another element, and hence it forms no compounds. Berylium has two electrons, and can give one of them to each of 2 fluorine atoms, thus completing two octets; and this is in agreement with the formula BeF_2 for this compound. But berylium has no tendency to combine with lithium, since no octets could be completed by such a combination. Now the electron shell of oxygen lacks two electrons of a complete octet, and these may be taken from 2 lithium atoms (forming Li_2O) or from 1 berylium atom (BeO). The electron shell of carbon lacks four electrons of being complete, it may give up two electrons to each of 2 oxygen atoms to complete their octets (forming CO_2) or it may take up four electrons from 4 hydrogen atoms to complete its own octet (CH_4). This is the first element which can either complete its own octet or give all of its electrons to another atom or group of atoms.

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[1] This idea was apparently first proposed by Parson, *Smithsonian Inst. Misc. Publ.*, **65**, 11 (1915); clarified and elaborated by G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916); and finally widely extended by Langmuir, *J. Am. Chem. Soc.*, **41**, 868, 1,543 (1919); **42**, 274 (1920); *J. Ind. Eng. Chem.*, **12**, 386 (1920). Similar views have been expressed by Wyckoff, *J. Wash. Acad. Sci.*, **9**, 565 (1919); Kossel, *Naturwissenschaften*, **7**, 339 (1919); Kirchoff, *Z. physik. Chem.*, **93**, 623 (1919), and others. In the treatment here given, no attempt is made to credit the various writers with their share in formulating this theory; and only the essential features are considered at all. Many of the interesting consequences of this work are available to elementary students who care to study the original papers, especially those of Lewis and Langmuir.

[2] Photographs of space models of these and other atoms are given by Foster in *Chem. Met. Eng.*, **23**, 690 (1920).

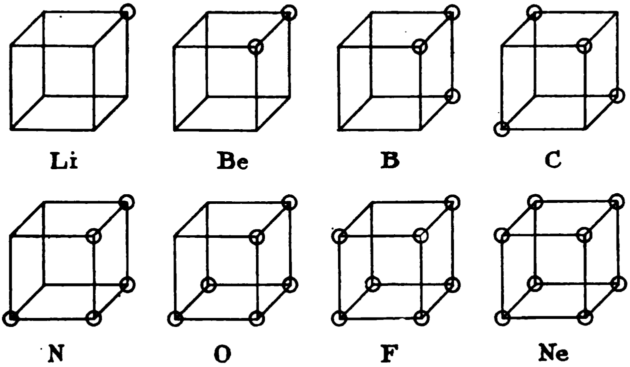

FIG. 54.—Arrangement of electrons around the atomic nuclei for elements in the first period of the periodic table. (*After Lewis.*)

Sharing Electrons.—When an element is not afforded an opportunity to complete its octet at the expense of some other atom or atoms, it may share a pair of electrons with another atom of its own kind. That is, 2 fluorine atoms may combine as shown in Fig. 55, if their octets have two electrons which exist in both octets at once. This explains the existence of a very stable molecule F_2. But this arrangement is less satisfactory, and less stable, than eight electrons for each octet. Hence this arrangement is readily abandoned in the presence of such elements as hydrogen or lithium which will give up an electron. It is generally true that chemical combination will take place by completing octets if possible, and by sharing pairs of electrons as second choice. The oxygen molecule is formed so as to contain two completed octets in which two pairs of electrons are shared, corresponding to two edges of the cube being in contact.

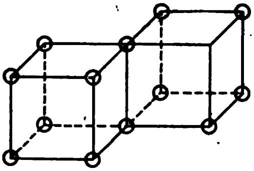

FIG. 55.—Electron arrangement in a fluorine molecule.

Sodium to Argon.—(Second period of the periodic table.) The first element after neon is sodium, which must have an electron arrangement similar to lithium if this is responsible for the chemical properties. The inner stable pair is completed; the octet is completed, and one electron is available for beginning a new octet outside of the first one. There is no tendency whatever for the ten electrons of the stable pair and the first octet to exert any effect upon the properties of sodium; they remain undisturbed by chemical processes, and only the single electron of the outside octet is active. This is true of all the elements; their properties depend only on the outside layer of electrons, not upon the inner layers, and no element starts to form a second octet until the octet under it is completely filled. Sodium has eleven electrons, two for the stable helium conformation, eight for the stable neon octet, and one in the new octet. It has no capacity for taking on seven other electrons, but readily gives up one to complete the octet of another element. Having lost this electron, it has 10 negative electrons and 11 positive charges in its nucleus; it is therefore positively charged, and such a structure is found in the free sodium ion in solution. Langmuir believes that this sodium ion also exists in the solid crystal, and that the chlorine atom has taken an electron into its octet from sodium even in a salt crystal, which consists of the *ions* held in a space lattice.

Magnesium has an arrangement of electrons in the outer shell like beryllium, aluminum like boron, and silicon like carbon, so far as the *outside* shell of electrons is concerned, and it is mainly this outside layer which governs the chemical properties of atoms. In silicon there is the tendency to give up four electrons (as in $SiCl_4$) or to take up four electrons (as in SiH_4), and the following elements, phosphorus, sulfur and chlorine, show a decreasing tendency to give up five, six, or seven electrons; together with an increasing tendency to take on three, two, or one and complete their own octets. Chlorine has 17 electrons, and by taking on one more (as in a combination with lithium or sodium) it completes its second octet and has the electron arrangement of argon. As in the case of fluorine, chlorine will share a pair of electrons with another chlorine atom; the electron arrangement in the outer shell of a chlorine molecule is the same as that shown in Fig. 55 for fluorine. In the simplest oxide of chlorine, oxygen (which lacks two electrons of completing its first octet) may share two pairs of electrons with 2 chlorine atoms, thus completing three octets in which certain electrons are forced to share in two octets at once. The arrangement is shown in Fig. 56.

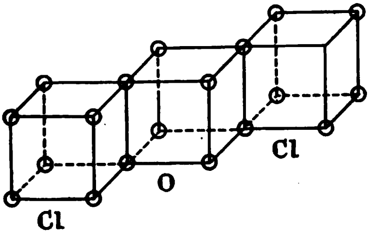

Fig. 56.—Electron arrangement in chlorine monoxide.

Continuing through the elements after argon, the first three, potassium, calcium and scandium, seem to follow along the same system as in the first two periods; potassium behaves much like sodium, calcium like magnesium, etc. But with the twenty-second element, titanium, some new set of influences seems to begin. Titanium is not like carbon or silicon, vanadium has properties widely different from phosphorus, chromium does not resemble sulfur in as many ways as it differs from it, and manganese bears little resemblance to chlorine. In all of these cases, there is some resemblance between elements in the columns of the periodic table, but there is more difference. The authors of this hypothesis of electron arrangement have not yet carried their speculations much beyond calcium, and we shall not attempt to do so. Let us examine some of the consequences of the electron structures assigned to the first 20 elements, especially in their bearing on the physical properties of compounds in which the electron arrangement is similar. We have seen already that elements of similar chemical properties have similar electron arrangements, and that the maximum number of electrons in an outer shell is eight, thus accounting for the periodic system.

Physical Properties and Electron Arrangement.—Let us take for comparison two molecules in which the total number of electrons is the same, and which according to this theory have the same structure so far as arrangement of electrons is concerned. Nitrous oxide and carbon dioxide each contain 16 electrons; each molecule is formed by the sharing of electrons in such a way that a central atom shares four pairs of electrons, two pairs with each of the adjacent octets. The arrangement is shown in Fig. 57. Each molecule contains three atomic nuclei, and there is thus great probability that their physical properties should be much alike *if the theory is correct.* There is not much other ground for expecting similarity except that their molecular weights are equal, and in other cases this is not found to bring about much resemblance of properties. Table 118 shows that there is great resemblance in physical properties of these two substances. Two other molecules of quite different chemical nature have also been found to have similar physical properties, nitrogen and carbon monoxide; and to have identical electron arrangements within the molecule, according to this theory.

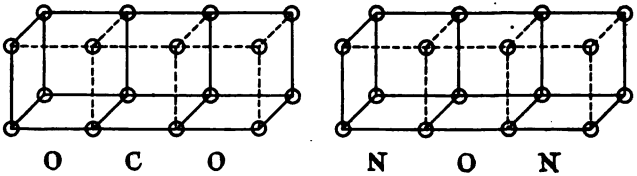

FIG. 57.—Electron arrangements of carbon dioxide and nitrous oxide.

TABLE 118.—COMPARISON OF PHYSICAL PROPERTIES[1]

Property	N_2O	CO_2
Critical pressures	75 atm.	77 atm.
Critical temperatures	35.4°	31.9°
Viscosity at 20°C	148×10^{-6}	148×10^{-6}
Heat conductivity at 100°C	0.0506	0.0506
Density of liquid at −20°	0.996	1.031
Density of liquid at +10°	0.856	0.858
Refractive index of liquid. D line, 16°C	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atm. 16°C	0.12×10^{-6}	0.12×10^{-6}

Isosterism.[2]—Atoms or atomic groups having within them the same number and arrangement of electrons are called isosteres. Thus neon, sodium ion and magnesium ion are isosteric; the first having a complete outer octet, the second having reverted to this form by the loss of its one electron to some other element, and the third by the loss of two outer electrons. Similarly, nitrate ions and carbonate ions, while their structures are somewhat complicated, have the same electron arrangement. Hence sodium nitrate and magnesium carbonate have the same electron arrangement, and it has been found that their crystallographic properties are identical.

A simpler example may be taken from elements which revert to the neon type. Oxygen can complete its octet by taking on two electrons, fluorine needs only one, neon none, sodium has one extra which it can yield to some other atom, magnesium has two extra electrons. The electron transfers just mentioned take place when these elements enter into chemical combination. Thus when sodium fluoride is formed, fluorine obtains its electron from the extra one in sodium, and the compound contains two completed neon octets. When magnesium oxide forms, the metal yields its two extra electrons to the oxygen octet which is thereby made complete, and this compound contains two completed octets of electrons. These substances should therefore be isomorphous if electron arrangement governs crystal structure, and they have been found to be isomorphous.

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[1] Langmuir, *Proc. Nat. Acad.*, **5**, 258 (1919).

[2] Langmuir, *J. Am. Chem. Soc.*, **41**, 1,548 (1919).

The reciprocal pair of compounds, sodium oxide and magnesium fluoride, each contain three completed octets, and should also, according to this theory, be isomorphous. The correctness of this statement has not yet been tested by experiment. Other predicted cases of isomorphism are potassium sulfide and calcium chloride, potassium chloride and calcium sulfide. The latter pair are related to each other as are sodium fluoride and magnesium oxide, the difference being that sulfur, chlorine, potassium and calcium complete their second octets of electrons in combining, while oxygen, fluorine sodium and magnesium complete the first octet only. Thus the lighter elements have the neon type and the heavier elements (S, Cl, K, Ca) have the argon type of electron arrangement.

Reviews of the subject of atomic structure have been written from time to time. Some of the most readily accessible ones are as follows:

A. S. Eve, *Science*, **40**, 115 (1914).
J. J. Thompson, *Sci. Amer. Suppl.*, **85**, 290, 306, 326, 346 (1918).
Harkins and Wilson, *J. Am. Chem. Soc.*, **37**, 1,396 (1915).
E. Rutherford, *Smithsonian Inst. Rept.*, **1915**, p. 167–202.
S. Dushman, *General Electric Review*, **20**, 186, 397 (1917).
E. Rutherford, *Proc. Roy. Soc. London*, March, 1914; *A* **97**, 1956 (1920).
K. Fajans, *Sci. Am. Supplement*, **81**, 82, 102 (1916).
Darwin, *Nature*, **106**, 51, 81, 116 (1920).

Papers on specific portions of the general problem of atomic structure, giving details, are generally difficult reading for beginners, but they are exceedingly helpful in obtaining a grasp of the subject. The following may be read with profit, even though some of the matter in them is not thoroughly understood after several readings of the text.

Lewis, G. N., *J. Am. Chem. Soc.*, **38**, 762 (1916).
Harkins, *Phys. Review*, **15**, 73 (1920), and earlier papers.
Langmuir, *J. Am. Chem. Soc.*, **41**, 868, 1,543 (1919); **42**, 274 (1920).
Wyckoff, *J. Washington Acad. Sci.*, **9**, 565 (1919).
Soddy, *Chemical News*, **107**, 97 (1913); *Nature*, **91**, 57; **92**, 399, 452 (1915).

CHAPTER XV

COLLOIDS. SURFACE CHEMISTRY

General.—Colloids are divided into two classes, which are fairly well represented by suspensions and jellies; or suspensoids and emulsoids; or sols and gels, as they are commonly called. In the first class are such mixtures as smoke and clouds (suspensions of solids or liquids in air), many dye solutions, turbid liquids and suspensions in general; in the second are most emulsions, jellies such as silicic acid, agar, gelatin, gum arabic, etc.

Suspensoids.—These consist of particles which are (usually) too small to be seen under a high power microscope, and which do not settle out upon long standing; to the unaided eye the suspensions appear perfectly homogeneous. It will be seen from this general statement that a sharp distinction between true solutions and colloidal suspensions has not been made. Indeed the solutions of very large molecules such as dye stuffs behave in many ways like colloidal suspensions, and colloidal suspensions have some of the properties of dilute solutions. The suspensions commonly encountered are of course composed of substances insoluble in the liquid in question; thus gold, platinum, ferric hydroxide, arsenious sulfide, vanadium oxide, sulfur, alumina, chromium hydroxide, silver iodide, prussian blue and similar substance form *hydrosols,* or aqueous suspensoids. As these substances are not absolutely insoluble in water, it will be understood that the suspending medium or dispersion medium is really a saturated solution of the substance in question, but this saturated solution differs but little from pure water.

Degree of Dispersion.—The diameter of particles concerned in suspensoid formation depends upon the method of preparation; thus gold suspensoids may be red, purple or violet according to the average size of particle produced, though the color also depends upon the concentration of colloid and its method of preparation. A red gold sol results from reducing a dilute gold chloride solution with carbon monoxide or with formaldehyde; a blue sol from reduction with hydrazine; either color can be prepared by striking an electric arc between gold wires under water, depending again upon experimental conditions, concentration of dispersoid produced, etc. Generally the red sols consist of smaller particles and the blue sols of larger ones. The actual diameter is best determined by counting the particles in a known volume of solution (by a method to be described presently), then evaporating a portion of sol and weighing the resulting deposit. From the number of particles per cubic centimeter, their weight, and the density of the dispersed substance, the average diameter is readily calculated. It should be borne in mind that diameters of individual particles in a sol may be very much larger and very much smaller than an average thus determined unless special precautions are taken to insure a nearly uniform size. This is accomplished by fractional settling, usually with the aid of a powerful centrifuge, or by the use of selective filters, called ultra-filters.[1] Diameter of particles can also be obtained from the density distribution of a sol under the influence of gravity, and in another way which will be described in connection with Brownian movement in a later paragraph.

Surface Phenomena.—According to Langmuir's theory of the structure of a solid (outlined in Chapter IV), an atom within a solid exerts its chemical attraction in all directions; an atom in a surface has unsatisfied attraction or chemical affinity reaching out into space, for a distance comparable with an atomic diameter at least, and this attraction may bring about condensation of molecules upon a surface. Adsorbed films of gases on glass are so explained. In a dispersed solid such as the solid phase of a suspensoid, a very large surface per unit weight of substance is exposed to the surrounding liquid. It is therefore to be expected that suspensoids will exhibit adsorptive power to an increased extent, that they will attract and hold whatever molecules may be dissolved in the dispersing liquid, and that the properties of these colloids will be greatly influenced by this adsorption. It should be remembered however, that the colloidal particles in very fine sols are of the order of 10^{-6} centimeters in diameter, while molecular diameters are of the order 10^{-8} centimeters, so that there are still some millions of molecules in the finest particles. Extent of surface is therefore of more importance than its curvature so far as adsorption is concerned.

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[1] Bechhold, *Z. physik. Chem.*, **64**, 328 (1908).

Dialysis.—It is readily demonstrated that suspensoids consist of particles which are much larger than ordinary dissolved molecules by placing them in vessels of parchment paper, thin collodion, animal membranes, etc., and suspending these vessels in pure water. Under such conditions salts, sugar, alcohol and ordinary solutes pass readily through the parchment, but suspensoids do not pass through at all. This offers a ready means of freeing suspensoids from salts, which often interfere with the stability of suspensions. It was in fact the difference in diffusing power which first led to a distinction between "crystalloids," which readily diffuse through membranes, and "colloids" which do not. This statement applies both to sols and to gels.

Dialysis is a slow process, requiring many days when a sol is to be freed from dissolved substances completely. It cannot, in general, be accelerated by immersing a sol in hot water, since this is likely to precipitate the sol. As dialysis depends upon diffusion of a dissolved substance through a membrane into a region where its concentration is lower, the rate of dialysis depends upon the area of membrane used and the difference in concentration between the inside and outside liquid. Hence a vessel composed entirely of membrane is used to enclose the sol, and a stream of distilled water is passed into the outer vessel at a sufficient rate. Toward the end of such a dialyzing process the difference in concentration of diffusing substance becomes very small, and the rate very slow.

Methods of Preparing Sols.—Reduction of a solution of gold chloride has already been mentioned; similar reduction of other salt solutions by suitable reagents has been employed for sols of silver, platinum and its related elements. Sols readily result when the vapor of a metal formed in an electric arc is suddenly chilled by immersing the arc in water. Sols of gold, silver, copper, platinum, carbon, etc., are prepared in this way. When electrodes of oxidizable metals are used, a sol results which is probably an oxide or hydroxide of the metal; this is the case with iron, zinc and aluminum; but these metals give a pure metal sol in non-oxidizing liquids such as hydrocarbons. In the latter case some carbon sol is probably formed at the same time as a result of reduction of the organic substance at the cathode.

Ferric hydroxide sol is formed on boiling a dilute solution of ferric chloride or acetate. This sol should be dialyzed to free it from salts if it is to be kept for a long time. Silver iodide, dissolved in strong potassium iodide solution, forms a suspensoid when the solution is poured into a large quantity of water. Sulfur dissolved in alcohol precipitates as a fine suspensoid when a large quantity of water is added. Sols of insoluble sulfides (As_2S_3, CdS, etc.) may be prepared by direct precipitation, followed by dialysis to remove the salt or acid formed.

Another method of forming sols is called peptization. Certain substances which dissolve in water as true solutes so act upon precipitates as to convert them into suspensoids, the most common case of inorganic sols being that in which a peptizing agent has an ion in common with the precipitate. Thus silver halides are "peptized," or converted into sols, by dilute silver nitrate or the corresponding potassium halide; sulfides, such as cadmium sulfide, zinc sulfide, mercuric sulfide and lead sulfide, are peptized by hydrogen sulfide; metallic oxides are peptized by strong alkali hydroxides. In some cases this is reversible, as in that of metallic sulfides which can be peptized by hydrogen sulfide, thrown down by boiling it out, again peptized by passing hydrogen sulfide into a suspension of the precipitate, and this process may be repeated over and over again.[1]

Determination of Molecular Weights.—Sols do not appreciably lower the vapor pressure or freezing point of the solvents in which they are dispersed; their osmotic pressures are either zero or very small, and hence their molecular weights are very high. It is uncertain whether osmotic pressure measurements carried out on these substances really represent the osmotic pressure of the colloidal substance itself, and not some contaminating solute, in spite of great care used in purifying the sols. Molecular weights so determined are often many thousands, and far from concordant. Doubtless such slight osmotic pressures or freezing point depressions as are observed are due partly to impurities. It will be clear from considerations to be given presently that colloidal particles are far larger than ordinary molecules, and that ordinary molecular weight methods are quite unsuited to studying them.

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[1] See Bancroft, *Brit. Assoc. Adv. Sci. Rept.*, **1918**, 5.

Viscosity and Density.—Densities of colloidal suspensions, calculated on the assumption that the sol is a mixture of solid particles in suspension in a liquid and without any effect upon it, agree with those based on experiment. This is not surprising in view of the small concentrations of suspended material usually encountered, as these are usually less than a tenth of 1 per cent. Sols generally have viscosities which differ but little from that of the pure suspending medium; but in some sols having a high percentage of suspended matter, the viscosity increases with colloid concentration more rapidly than can be explained by allowing for the volume of colloidal material.

Electrical Properties.—Sols have a very small effect upon electrical conductivity, and this is in all probability due to traces of electrolyte adsorbed on the particles.[1] Either on account of adsorbed ions or as a result of electric charges due to friction beween a particle and its surrounding liquid, suspensoids appear to be charged. When placed in an electric field, some suspensions move toward the anode, and are therefore negatively charged. Among these may be mentioned most colloidal metals, arsenious sulfide and silver iodide. Other colloidal suspensoids move to the cathode and are therefore positively charged; most hydroxide sols are in this class. The belief that adsorbed ions are responsible for charges is supported by the precipitation of positive sols by negative sols. The opposite belief is supported by experiments in which a colloidal substance is held stationary in an electric field, when water is caused to move past the colloid. Arsenious sulfide moves toward the anode when the water is stationary; if the sulfide is held stationary (as in a membrane), water flows toward the cathode. Thus the displacement of one substance relative to the other is the same no matter which one is made stationary. This movement in an electric field is applied industrially in purifying china clay, in tanning, in medicine, and for separating colloidal and non-colloidal mixtures.[2] The mode of action is similar to that in the Cottrell precipitator for smoke and dust, in which fine particles suspended in air are caused to precipitate on a charged netting or set of chains.

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[1] Whitney and Blake, *J. Am. Chem. Soc.*, **26**, 1,339 (1904).

[2] Briggs, *Rept. Brit. Assoc. Adv. Sci.*, **1918**, 39.

The Ultra-microscope.—This instrument does not render particles *visible* which are invisible in an ordinary high power microscope, but it shows that such particles are present by a bright spot of light radiated from each particle. Nothing whatever as to the size or color or shape of a particle is learned from its effect upon the eye when viewed through an ultra-microscope, yet the apparatus is justly entitled to its name, since it shows the presence of a particle which cannot be seen at all in an ordinary microscope. A rough illustration of the principle on which it is based is afforded by the beam of light from a projection lantern in a darkened room, the so-called Tyndall effect. This shows particles of dust or smoke suspended in the air which are quite invisible when the room is thoroughly lighted; but does not show the color of the particles. A beam of light passed through clean air shows no such effect. The ultra-microscope merely magnifies highly a small portion of such an illuminated area of a suspension in a liquid medium, which is made so dilute that light radiated from each particle reaches the eye without interference from some other particle, as shown in Fig. 58. Under similar conditions a concentrated suspension gives only a uniformly bright field in which no individual particles are rendered visible.

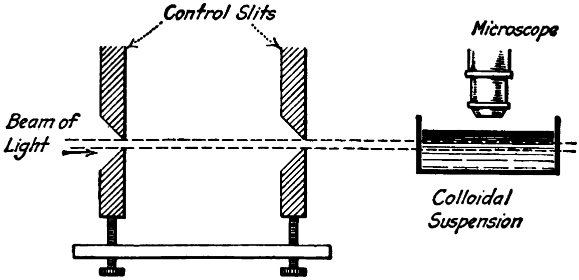

FIG. 58.—Diagram of an ultra-microscope.

A particle 10^{-5} centimeters in diameter is invisible under the highest power of a microscope, but the effect of such a particle is clearly seen under an ultra-microscope. Particles far smaller in diameter than a wave length of visible light are able to show their effects by radiating a beam of light under the ultra-microscope, and the number of such particles in an illuminated volume may be counted. When the size of field under the microscope is known, and the depth of illuminated area is measured and regulated by a micrometer slit between the arc light and vessel containing a sol, a count of the spots of light in such a field gives the number of particles in a known volume. Even with very dilute sols it is often necessary to dilute them with large quantities of pure water before a count is possible. For this dilution ordinary distilled water is quite unsuited, as it contains thousands of visible particles in a drop. Specially prepared "optically empty" water is required, and its preparation requires special methods.

The size of particle detected by an ultra-microscope depends chiefly upon the intensity of illumination; the lower limit is not far from 10^{-6} centimeters, which is about 2 per cent of the wave length of visible light.

Brownian Movement.—Molecules in a liquid are in rapid though tumultuous motion of the kind outlined in connection with the kinetic theory of gases. A colloidal particle is very large compared to the diameter of a single molecule, and it is continuously bombarded on all sides by great numbers of molecules. Occasionally the pressure due to this bombardment is for the moment greater on one side of the particle than on the other, and the particle is urged forward until a new distribution of impacts hurls it in another direction. The excursions due to these movements depend mainly on the size of the particles, and the movements correspond exactly with that predicted by the molecular theory.

Here we have reproduced in a way visible to our eyes the random unordered continuous motion of molecules postulated in connection with the kinetic theory of gases. This motion takes place as a result of impacts with real molecules, but it makes a colloidal particle behave as if it were a single molecule. This motion was first observed by the botanist Brown on plant cells which were visible in an ordinary microscope; the movement was little more than an irregular oscillation, whose real cause remained long unsuspected. From equations based upon the kinetic theory it may be shown that the amplitude of this vibration is directly related to the diameter of the particle and the viscous resistance of the suspending medium. Thus what is a slow oscillation effect produced upon a plant cell or small bacillus in an ordinary high power microscope becomes for a much smaller colloidal particle a lively zig-zag motion, as shown by the cone of light radiated from it in an ultra-microscope.

A reliable method of determining the size of suspended particles is based upon their Brownian movement, the equation for which is used in another way in the next paragraph. In this equation the radius of a particle may be determined if we assume a value for Avogadro's number of molecules in a gram molecular weight of gas; or from counting particles and an analysis of the sol we may determine the radius, perform the reverse calculation, and compute a value of Avogadro's number. The latter procedure is more interesting, though it will be evident that the calculation may be reversed if desired.

Brownian Movement and Avogadro's Number.—A relation may be derived between the intensity of Brownian movement, the radius of the particle, the viscosity of the dispersing fluid and the number of molecules of gas in a gram molecular weight. Since colloidal particles are bombarded by molecules in a wholly random way, they will have the random motions of a large gas particle, and will behave as such. Upon this assumption, the equation, in terms of the mean displacement d in a unit of time t, is

$$\frac{d^2}{t} = \frac{RT}{3N\pi r\eta}$$

where r is the radius of a particle and N is Avogadro's number, η being the viscosity of the liquid suspending medium. Experiments based upon observation of displacements in small time intervals lead to values of Avogadro's number between 6.2×10^{23} and 6.9×10^{23}, in good agreement with other methods.

Distribution of Particles Under the Influence of Gravity.—A suspension of heavy particles tends to separate out the solid under the influence of gravitational attraction, and is partially prevented from so doing by Brownian movement, in much the same way that molecules of the atmosphere are attracted to the earth by gravity and prevented from settling upon it by the intensity of their molecular motion. The equation expressing the variation in density of the atmosphere with the altitude contains N, the number of molecules in a gram molecular weight. A colloidal suspension of particles of uniform size which has reached settling equilibrium distributes itself in the same way that the atmosphere is distributed under the action of gravity, thus reproducing within reasonable space the effect for which the atmosphere requires several miles of altitude. From determinations of the number of particles per cubic centimeter at equilibrium, the variation of density with altitude may be established, and used to calculate a value of Avogadro's number N. If n_1 is the number of particles per unit volume at a level which we may call zero height, and n_2 is the number at another level h centimeters above the first one, the equation for change of concentration with h is

$$2.303 \log \frac{n_1}{n_2} = \frac{Nmgh}{RT}$$

where m is the difference in mass between a colloidal particle and the volume of solvent it displaces, g is the acceleration of gravity, and N is Avogadro's number. Investigations based upon this equation[1] lead to a value for N of 6.8×10^{23}.

Precipitation of Colloids.—As has been mentioned before, most suspensoids are electrically charged, probably as a result of adsorbed ions on the surface of the suspensoid particles. Ionic adsorption is a selective process, some ions being more strongly adsorbed than others. When to a positively charged sol a solution is added containing readily adsorbed negative ions, these neutralize the electric charge of the particles so that they no longer repel each other, and coagulation or precipitation takes place. It has lately been recognized that this ionic adsorption is highly specific, both in regard to the colloid and the ions. A general rule, to which there are occasional exceptions, is that ions of higher valence are more strongly adsorbed (and therefore more effective in producing precipitation) than ions of lower valence. Thus for most negatively charged suspensoids, ferric salts, aluminum salts and trivalent cations in general are most effective as precipitants, that is, produce coagulation when added in the smallest concentrations; lead and barium salts next, then heavy monovalent ions such as silver, and finally the alkali ions are

[1] Perrin, 1913. See Dushman, *Gen. Elec. Rev.*, **18**, 1,159 (1915).

least effective. Similarly, positively charged sols are more readily precipitated by sulfates than by monovalent anions at equivalent concentrations. Among the latter the order of decreasing precipitating effect[1] is sulfocyanate, iodide, chlorate, nitrate, chloride, acetate, phosphate, sulfate, for albumin colloid; but the precipitating power of these ions is in the reverse order for some other colloids.

Precipitation also takes place when a positively charged sol is added to a negatively charged sol, each neutralizing the charge carried by the other. It does not follow that a chemical compound is formed, though the coagulated material may seem to be a compound. For example, ferric hydroxide sol precipitates arsenious sulfide sol, but does not form ferric thioarsenite.

Protective Colloids.—Certain substances have a conspicuous property of stabilizing colloidal suspensions. Thus a dispersoid of silver chloride is maintained in a stable state by gelatin in a photographic film, and the success of a film is entirely dependent upon its retaining a uniform dispersity of this silver chloride. Gelatin and other protein substances are in fact the most common protective agents, though gum arabic, dextrin, starch, casein and soap are also effective to a greater or less extent, and tannic acid is used to protect the graphite suspensions used as lubricants. The peptizing action mentioned in a previous paragraph is not thought to be a protective colloidal action, but an adsorption effect of a common ion. There is no reason to doubt that adsorption is also active in the mechanism of protective colloids, though a simple and quite plausible explanation is that the protective substance coats the suspended particles with a very thin layer of itself. Substances which are effective in this respect are themselves able to form very stable gels.

Emulsoids.—These differ from suspensoids in that both phases are liquid, and the ratio of dispersed phase to dispersing medium is much larger. In the sols already considered the dispersed phase was seldom present in greater quantity than a fraction of 1 per cent; emulsoids have been prepared in which the dispersed phase was 99 per cent of the whole, only about 1 per cent being the continuous or dispersing phase. Emulsions of oil in water (when the disperse phase amounts to one part per thousand) and similar dilute emulsions are properly considered as suspensoids, and are not included in this discussion.

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[1] Bancroft, *J. Physical Chem.*, **19**, 352 (1915).

Emulsions containing large percentages of disperse phase are stable only when the interfacial tension between the phases is low,[1] and this lowering of surface tension is sometimes brought about by dissolving soap or other substance in the dispersing medium.

Concentration in Surfaces.—It is a general law that substances which lower the surface tension of a solution accumulate in the surface, producing there a higher concentration of solute than is present in the bulk of liquid. Any substance which will lower the surface tension may aid as an emulsifying agent. The relation between u, the excess of solute in a surface, c, the concentration, and the rate at which surface tension changes with concentration is

$$u = -\frac{c}{RT}\frac{d\gamma}{dc}$$

which is called the Gibbs equation. From this equation it will be seen that if $\frac{d\gamma}{dc}$ is positive (surface tension is increased by the solute), u is negative, and there is no accumulation of solute in the surface, but a deficiency of it; when the solute lowers the surface tension, $\frac{d\gamma}{dc}$ is negative, and u is positive, that is, solute accumulates in the surface in excess. If a froth is formed on such a liquid in which the surface tension has been lowered, excess solute will be found in the froth.

In moderately strong solutions of substances which depress the surface tension, the surface itself consists of a layer *one molecule deep*[2] of the dissolved substance, and there is never a transition layer in which the concentration varies progressively at points further from the surface into the solution. The amount of solute required to form this layer may be calculated from the Gibbs equation, and from this quantity of solute in the surface layer may be calculated the diameter and cross section of the molecules forming the layer.

With solutions of inorganic salts, where the surface tension is greater than that of water and increases linearly with the concentration, there is a deficiency of solute in the surface layer proportional to the concentration. This surface layer therefore consists of water molecules in excess.

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[1] Hatschek, *Rept. Brit. Assoc. Adv. Sci.*, **1918**, 17.

[2] Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 251 (1917).

Surface Tension and Emulsion Formation.—It has been shown[1] that lowering of surface tension is produced by those substances which aid emulsification, and that therefore a lowering of surface tension is essential to the formation of stable emulsions. The first sodium salt of the series of fatty acids to produce appreciable lowering of surface tension when it is added to water is sodium laurate, and this is the first salt in such a series to aid appreciably in forming emulsions of oil in water. Further experiments have shown a proportionality between emulsifying power and decrease of surface tension, so far as emulsions of oil in water are concerned.

Structure of Emulsions or Gels.—Viscous emulsions and gels have the same structure; a stiff jelly is often convertible into an emulsion by heating, and it returns again to the state of jelly after cooling. In each case microscopic droplets of one liquid phase are completely surrounded by a continuous film of the other liquid phase. It is not necessary that the continuous phase be present in greater quantity than the dispersed phase; a cross section of an emulsion in which the disperse phase is present in excess might look something like a section through a cake of honey, with thin films of continuous phase (represented by the wax cell walls) surrounding droplets of dispersed phase. It is only necessary that there be enough dispersing phase to form a *continuous* film between each droplet and the next neighbors to it. Gelatin gel is considered as a dilute solution of gelatin dispersed in a more concentrated one, the stiffness of such a jelly being due to resistance to shearing of the stronger solution. That this is not incompatible with the properties of liquids in general is shown[2] by the fact that stiff non-flowing gels have been prepared in which 99 per cent of mineral oil is dispersed in 1 per cent of a soap solution. The oil is the disperse phase, not the soap solution; as may be shown by adding a drop of oil to such a gel. If oil were the dispersing medium (continuous phase), it should spread through the whole gel; but it remains as a single drop in with the smaller droplets.

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[1] Donnan and Potts, *Kolloide Ztsch.*, **9**, 159 (1911).

[2] Pickering, *J. Chem. Soc. London*, **92**, 2,001 (1907).

Gels in the Ultra-microscope.—Gelatin and other gels show under the ultra-microscope a slight Tyndall effect which increases with concentration; but these gels do not show individual particles as in the case of sols. Such light as is seen in an ultramicroscope is probably due to a difference in index of refraction of the liquid phases forming a gel. There is no Brownian movement of the droplets of disperse phase. In very dilute dispersions of oil in water, Brownian movement is observed, but these are not properly considered gels, since the quantity of disperse phase is very small, and these emulsions have the property of suspensoids to a far greater extent than they resemble gels.

Viscosity of Emulsoids.—Emulsoids have viscosities which, even for very dilute gels, are much higher than that of the "solvent," and which seem to depend upon the rate of shear within the fluid dispersing medium. No satisfactory theory relating to the viscosity of colloids has been developed, but it is known that very slight changes in a gel produce a marked effect upon its viscosity, and hence viscosity measurements are a delicate means of tracing such changes. About all that can be deduced, however, is that a change has taken place, the nature of which is matter for speculation or empirical interpretation. Use of such methods is extensive in the rubber and nitrocellulose laboratories,[1] where the age of an emulsoid is a very important factor in determining its properties. Lack of a satisfactory theory does not interfere with the use of these measurements as control methods.

References.—Complete and thorough reviews of the science of colloidal chemistry are given in the reports of the British Association for the Advancement of Science for 1917 and 1918. Many of the facts in this chapter have been taken from this report. The industrial applications of colloid chemistry are there reviewed briefly, with full references to the original sources of information, of which over a thousand are given in the report. There are, in addition, several text books of colloid chemistry available in English. Practical applications of colloid chemistry to lubrication, water proofing, plasticity of clays, and colloidal fuel are reviewed in *J. Ind. Eng. Chem.*, **12**, 434 (1920); the setting of cement as influenced by its colloids is discussed in the British Association report. Reference should also be made to Bancroft's "Applied Colloid Chemistry" in this series of text books.

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[1] Hatschek, *Rept. Brit. Assoc. Adv. Sci.*, **1917**, 22.

CHAPTER XVI

ELECTROCHEMISTRY

Chemical reactions at electrodes, and the method of conduction of solutions of ionized substances, have been considered in an earlier chapter. In this chapter we shall be concerned mainly with another aspect of electrochemistry, the potentials of electric cells or batteries, and the energy to be derived from these cells. The energy of any electric process is the product of potential and quantity of electricity, or the product of potential, current and time. In the usual units of volts, amperes and seconds, the energy unit is a volt-ampere-second or joule; 4.182 of these units being equivalent to one small calorie.

Consider the Daniell cell, which consists of a rod of zinc dipping into zinc sulfate solution and a rod of copper dipping into copper sulfate solution, the two solutions being in contact. In conformity with the usual method of writing such a cell, it may be described thus:

$$Zn, ZnSO_4, CuSO_4, Cu.$$

Faraday's law states that when two faradays of positive electricity are passed through such a cell from left to right, two equivalents or one atomic weight of zinc passes into solution as zinc ion and an atomic weight of copper is deposited, or if the electricity is passed in the other direction, an atomic weight of copper dissolves off the copper electrode and an atomic weight of zinc deposits.[1] Faraday's law says nothing as to which of these reactions will occur or whether either reaction will of itself supply electric energy. If zinc dissolves, copper deposits and electric energy is supplied by the battery to an outside mechanism; the reverse process will not take place unless energy from an outside source is supplied to the battery.

[1] The Daniell cell acts as a reversible cell in a potentiometer, that is for very small currents; for large currents gas would be evolved at the cathode in place of part of the zinc which should otherwise deposit. This cell could not, therefore, serve as an efficient storage battery.

When a copper rod is placed in a solution of zinc sulfate, no chemical reaction occurs. But when a rod of zinc is placed in copper sulfate, the rod is attacked, and copper is precipitated upon it. Thus we see that the precipitation of copper, with the solution of an equivalent quantity of zinc, will take place of itself. The same process will therefore take place of itself in an electric battery producing the same chemical change. The only difference between a battery and a rod of zinc dipped into copper sulfate is that in the battery, solution of zinc takes place in one part of the system, and copper is precipitated in another part. The fact that zinc will precipitate copper from its solutions, while copper will not precipitate zinc from its solutions, is often expressed by saying that zinc has a higher solution pressure than copper. A better expression is that zinc has a higher solution potential, or electrode potential than copper. When the elements are arranged in the order of decreasing electrode potential, the "electromotive series" mentioned in inorganic chemistry is obtained. The elements high in this series have high electrode potentials, and will in general displace from solution those below them. Thus all of the metals above hydrogen in this series will displace hydrogen from acids, while those below it will not. This may also be expressed by saying that those metals having a higher electrode potential than hydrogen will displace it from acids in solution.

Upon writing the chemical equation for the Daniell cell,

$$Zn + CuSO_4 = Cu + ZnSO_4,$$

we see that the net effect of its operation is the transfer of positive electricity from copper ions to zinc ions. This will be clearer if the equation is written in ionic form,

$$Zn + Cu^{++} = Zn^{++} + Cu.$$

During the operation of a Daniell cell, positive electricity is transferred from copper ions to zinc ions by passing the charges through a wire connecting the electrodes. When this occurs, an electric current is passing through the wire, and may be made to perform work as it flows.

We shall be concerned only with the *maximum potential* of such a system, since the product of this maximum potential and the quantity of electricity is the maximum work available from the chemical change involved. In order to obtain this maximum potential it is necessary that the cell operates very slowly, and that the concentration of each solution remains uniform. To determine this maximum potential, the battery is opposed to a potential from another source which is substantially equal to the electromotive force of the battery, in the way explained in the next paragraph, and illustrated in Fig. 59.

A potentiometer is an arrangement for comparing one electromotive force with another which is already known. Suppose a storage battery, whose electromotive force is unknown, to be connected to the ends of a uniform wire 10,000 mm. long and of very high resistance. The potential drop along this wire is uniform, but unknown. In order to determine the electromotive force of the storage battery, and hence the potential drop per millimeter of wire, a "standard cell" of known electromotive force is placed in position *e*, in series with a galvanometer, and contact is made at such a point *c* that there is no deflection of the galvanometer. Commonly the Weston cell, electromotive force 1.01872 volts, is used, but any other battery of known electromotive force will serve. The potential of the storage battery bears the same relation to that of the standard cell as *ab* does to *ac;* for since there was no deflection of the galvanometer when contact was made at *c*, there was no current flowing under these conditions, and therefore the electromotive force of the standard cell was opposed by an exactly equal one supplied by the storage battery. The wire *ab* being of uniform resistance, only the part *ac*/*ab* of the total potential from the storage battery was required to be equal to that of the standard.

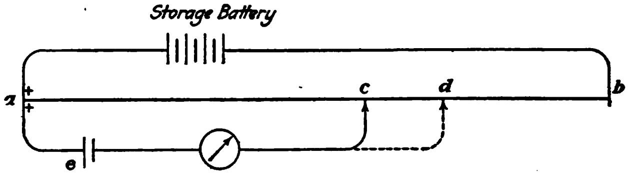

FIG. 59.—Potentiometer diagram.

Now remove the standard cell and place in its position the unknown Daniell cell, and find such a point of contact *d* that there is no current flowing through the galvanometer. Then the new cell has an electromotive force which is to that of the standard as *ad* is to *ac*.

Hydrogen-chlorine Cell.—Any chemical reaction involving ions can be made a source of electric energy if the reaction can be made to take place at two different parts of a system through a transfer of electric charges from one place to another. If the reaction is a spontaneous one, it will give rise to electric energy under these conditions; otherwise it may be made to occur by supplying electrical energy to it from some outside source. For example, the spontaneous union of hydrogen and chlorine to form hydrochloric acid may be made to serve as a source of electric energy, provided the transfer of electric charges is properly arranged. Hydrogen molecules are not electrified, nor are chlorine molecules; in a solution of hydrogen chloride, the main constituents are hydrogen ions and chloride ions. The chemical reaction $H_2 + Cl_2 = 2HCl$ (in solution) may be made to take place in two steps, one of which occurs at a hydrogen electrode, $H_2 + 2 \oplus = 2H^+$, using the positive charges from the chemical reaction at a chlorine electrode, $Cl_2 = 2Cl^- + 2 \oplus$, where a faraday of positive electricity is denoted by $\oplus$.

A hydrogen electrode consists of a plate of platinum dipping into an acid solution, and in contact with hydrogen gas. A slow current of gas is bubbled over the plate in order to stir the acid around it and keep the electrode thoroughly saturated with hydrogen gas. A chlorine electrode is prepared in the same way, and the two electrodes are dipped into hydrochloric acid. The electromotive force so set up is measured with a potentiometer as explained above. A diagram of the apparatus is shown in Fig. 60.

Operation of a Cell.—When a hydrogen-chlorine cell is allowed to operate, the effect at each electrode during the production of an electric current is just the opposite of that occurring during electrolysis. At the left hand electrode hydrogen goes into the solution as hydrogen ions, chlorine enters at the other electrode as chloride ion, and the current passes in the opposite direction to the electrolyzing current. This is therefore a cell, which may either produce electricity and form hydrogen chloride in solution from its elements, or use electricity from an outside source in decomposing hydrogen chloride into its elements. For the operation in either way, electrochemical reactions take place at each electrode which are strictly in accordance with Faraday's law, two faradays (2 × 96,500 coulombs) being required to decompose two mols of hydrogen chloride into one mol of chlorine and one of hydrogen, or two faradays being produced when one mol of hydrogen and one of chlorine unite to form two mols of hydrogen chloride in solution. During the production of electricity by the cell, the reaction at the chlorine electrode is

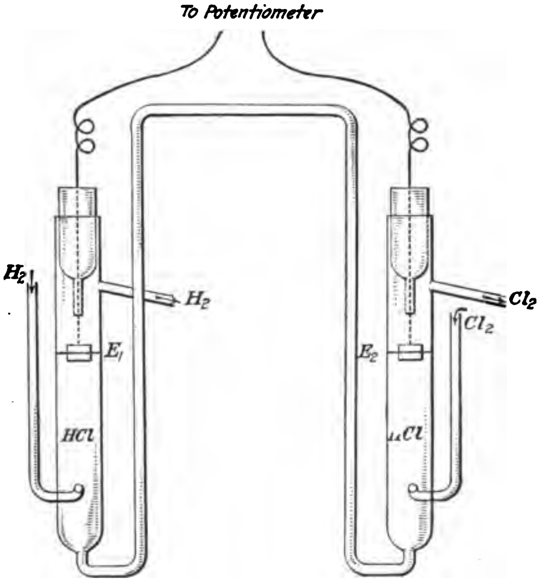

FIG. 60.—Diagram of a cell for deriving electric energy from the union of hydrogen and chlorine.

$$Cl_2 = 2Cl^- + 2 \oplus$$

where the symbol $\oplus$ is used to denote a faraday of positive electricity which is given to the electrode. It will be seen that this is just the reverse of the reaction occurring during electrolysis. At the hydrogen electrode a reaction occurs which causes positive electricity to enter the solution, corresponding to the chlorine reaction with gives positive electricity to the electrode. The hydrogen reaction is

$$H_2 + 2 \oplus = 2H^+,$$

which is again the reverse of the electrolytic reaction.

The passage of two faradays of positive electricity through this cell from left to right, for a cell arranged as in Fig. 60, causes the formation of two mols of hydrogen chloride, a chemical effect which corresponds to a spontaneous process. When chlorine and hydrogen gases are mixed, they combine with the evolution of much energy. When they are combined by means of an electric cell, this energy appears in the form of electricity. If E is the maximum electromotive force of this cell, as measured on a potentiometer, the electric energy produced in forming two mols of hydrogen chloride is $2EF$, where F denotes 96,500 coulombs of electricity. This is the maximum work obtainable by this chemical process; it is also the maximum work of any other process which forms hydrogen chloride from its elements and introduces it into a solution.

The above statement of maximum work applies when E is the electromotive force measured on a potentiometer, that is, the maximum electromotive force. If the potential is not opposed by a substantially equal potential, current will flow rapidly from the cell, and the solutes produced by electrolysis will not diffuse into the bulk of solution as rapidly as formed. Under these conditions the electromotive force developed is less than the maximum available potential for slow operation of the cell. The maximum work produced electrically is $2EF$ when E is the maximum potential, but a smaller potential, and hence a smaller quantity of electric work, corresponds to the operation of a cell in which the concentration is not uniform. Such a cell is said to be partly polarized; polarization is the accumulation around an electrode of the products of electrochemical reactions.

Formulation of Cells.—In this chapter we shall consider only reversible cells, that is, cells in which by passing an electric current in the reverse direction, the chemical effects attending its operation may be reversed. We shall consider as the electromotive force of a cell its maximum electromotive force as determined by a potentiometer, that is, we shall consider a cell as operating so slowly that each electrode is at all times in equilibrium with the solution around it. Solutions are considered to be present in large quantity, so that no appreciable change in concentration takes place in each one as a result of operating the cell. This is accomplished in laboratory practice by passing only a very small quantity of electricity, so that concentration effects are avoided, but it is convenient in discussing cells to imagine a very large cell, and pass through it one or two faradays of electricity corresponding to the production of a mol of dissolved substance. When only a very small quantity of electricity is passed through a cell in laboratory practice, it is clear that great purity of chemicals is required, otherwise the potential measured may be caused by a minute quantity of an unsuspected impurity sufficient to give an electrode reaction quite different from that which the cell is supposed to give. Cells are therefore set up in duplicate or triplicate and checked against one another frequently, to avoid this possible error.

The various parts of cells are separated by commas, which indicate points at which there is a difference of potential developed. This will be explained in detail presently. Denoting by M an inert metal,[1] the cell discussed above would be written

$$M + H_2(\text{ 1 atm.}),\ HCl\ (0.1\ m.),\ M + Cl_2\ (1\text{ atm.})$$

and the chemical reaction corresponding to two faradays of electricity is

$$H_2 + Cl_2 = 2HCl\ (\text{in } 0.1\ m.)$$

A *reversible* process is one which occurs in such a way that a substantially equal force is opposed to the one operating. For it is only in this way that the maximum work is obtained. Such a process may be reversed by a quantity of work which is only infinitesimally greater than the work obtained from it. When any change occurs rapidly, and without being opposed to a substantially equal force, the quantity of work done during the change is smaller by a finite amount than that required to reverse the process. Of course the process may be reversed, but only by expending upon it more work than it generated, therefore with a net loss of work in the surroundings of the system.

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[1] The presence of an inert metal at any gas electrode is always understood, though in formulating cells it is not always written down. For example, Cl_2, Cl^- means that an inert metal is dipping into a solution where chloride ions are present, and is in contact with chlorine gas at the specified pressure. It would of course be impossible for a gas alone to function as an electrode, for metallic conduction to and from it is necessary.

Maximum Electrical Work Available from a Cell.—Electromotive forces determined as outlined in the previous paragraph are the maximum potentials which may be developed by a given chemical change. The quantity of electricity involved in a chemical reaction is strictly that demanded by Faraday's law of electrolysis. Hence the electrical work done in such cells is the product of quantity of electricity and maximum electromotive force, or it is the maximum electrical work obtainable from any given chemical change. It is a fundamental law of nature that the maximum work derivable from a process carried out reversibly is independent of the method of carrying out the process. For a given reversible process carried out by a path giving the larger quantity of work and reversed by the path requiring a smaller amount of work, thus restoring the operating system to its original state, would otherwise result in *creating* a quantity of work which is the difference between that of the two paths, and this is impossible.

Whenever, therefore, a given chemical change may be brought about by passing n faradays through a cell of electromotive force E, the maximum electrical work of this process is the product of quantity of electricity and potential, or EnF. If this same chemical change, involving the same initial and final states of the system under consideration, is brought about in two different cells, each requiring the quantity of electricity nF, then if E_1 and E_2 are the electromotive forces of these two cells, $E = E_1 + E_2$, since $EnF = E_1nF + E_2nF$ according to the law of conservation of energy. In case the quantity of electricity involved is not the same in all three cells, it should be noted that it is EnF which is equal to $E_1n_1F + E_2n_2F$, whence if two faradays are involved in producing a change in the first cell, and one in each of the two which produce this change in steps, $E = \frac{E_1+E_2}{2}$.

These considerations are helpful in calculating electromotive forces of cells which cause a given change of state to occur in steps, each step being produced in a separate cell. The maximum work available from a given change in the state of a system is independent of the path by which this change is brought about, whether it involves a single step or several different steps; the same maximum work is always obtainable from a given change in state. It does not follow that the maximum work is always obtained, for a process may be brought about by an inefficient (irreversible) path not giving the maximum available work. The decrease in ability of a system to do work is the same as if the maximum work had been done, however.

Sign of Electromotive Force.—We shall pass positive electricity from left to right through a cell as written, and in all operations of cells consider that positive electricity so passes, regardless of the actual tendency of the cell. When a cell operates *of itself* in such a way that positive electricity does pass through it from left to right, its electromotive force is called positive; when an outside potential is required in order to force positive electricity through it from left to right, its electromotive force will be called negative.[1] Thus when we write

$$H_2\ (1\ \text{atm.}),\ HCl\ (0.1\ m.),\ Cl_2\ (1\ \text{atm.});\ E = +1.4881\ v.,$$

this indicates the tendency of positive electricity to pass of itself through the cell from left to right. Then at the left hand electrode the reaction corresponding to 1 faraday is

$$\tfrac{1}{2}H_2 + \oplus = H^+$$

and the cathode reaction on the right is

$$\tfrac{1}{2}Cl_2 = Cl^- + \oplus$$

and the sum of these reactions is the formation of hydrochloric acid into a solution. Since hydrogen chloride will form from hydrogen and chlorine, and since the gas so formed will dissolve in water, both of these processes are able of themselves to occur without the aid of outside energy. A positive electromotive force indicates that the cell will supply electricity during its operation, at the expense of the chemical energy evolved during a reaction taking place in the cell.

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[1] This is the convention adopted by Lewis, *J. Am. Chem. Soc.*, **35**, 1 (1913), and commonly used in American publications. European electrochemists employ the opposite convention. The usage here followed is in accord with that in the papers to which reference is made in this chapter.

It should be noted that by writing the cell in the opposite order and passing positive electricity through it from left to right, chemical reactions occur which are the opposite of those just given, and hydrogen chloride is decomposed into its elements. This is not a spontaneous process; it requires the use of outside energy. In the formulation of this cell, the facts just given are indicated as follows:

$$Cl_2 \text{ (1 atm.)}, \text{ HCl } (0.1\ m.), \text{ } H_2 \text{ (1 atm.)}; \ E = -1.4881\ v.$$

This is equivalent to saying that an outside electromotive force of at least 1.4881 volts is required to pass positive electricity from left to right through this cell.

Electrode Potentials.—There is at the junction between an electrode and a solution a tendency (positive or negative) for positive electricity to pass from *electrode to solution;* which tendency depends upon the electrode material, the concentration of the ion formed or destroyed in solution by the passage of electricity, and the temperature. In the cell just given[1] the separate tendencies at each electrode may be represented by

$$M + H_2 \text{ (1 atm.)}, \text{ HCl } (0.1\ m.); \ E_1 = x$$

and

$$M + Cl_2 \text{ (1 atm.)}, \text{ HCl } (0.1\ m.); \ E_2 = y.$$

In the cell under consideration,

$$H_2 \text{ (1 atm.)}, \text{ HCl } (0.1\ m.), \text{ } Cl_2 \text{ (1 atm.)}; \ E = 1.4881,$$

the total electromotive force as measured is the difference between x and y of the two halves of the cell, for y corresponds to the passage of positive electricity from electrode to solution; and in the actual cell positive electricity passes in the opposite direction. The total electromotive force of the cell is therefore $E = x - y = 1.4881$, which may be considered as the difference of two *electrode potentials.* One of these electrode potentials represents the tendency of positive electricity to pass into solution upon hydrogen ions, and is sometimes called the electrolytic solution tension of hydrogen; the other represents the tendency of positive electricity to pass from electrode to solution with the formation of chlorine gas from chloride ions. In general, the electromotive force of any cell containing only one solution may be computed from the difference of its two electrode potentials.

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[1] Lewis, *J. Am. Chem. Soc.*, **35**, 21 (1913).

The preparation of a table of electrode potentials is therefore a matter of importance. But as mentioned above, the electrode potential depends upon the concentration of solute already in the solution, and, in the case of electrode reactions involving gaseous substances, upon the pressure of the gas. This pressure is understood to be the partial pressure of the substance involved in an electrode reaction, not the total pressure. A table of *normal electrode potentials* or specific electrode potentials, representing the tendency of a metal to pass into a solution where the concentration of its ion is one molal, may be prepared in terms of the potential of any one electrode. It will be understood that a voltaic cell always consists of two electrodes, and that its potential depends upon the difference between the tendency of positive electricity to pass from electrode to solution at its anode and at its cathode.

It is now customary to assume the electrode potential of hydrogen gas at a partial pressure of one atmosphere, in contact with a metal electrode dipping into a solution one molal in hydrogen ion, as zero, and to refer the potential of all other electrodes to this arbitrary zero. This convention does not mean that there is no tendency for the reaction $\frac{1}{2} H_2 + \oplus = H^+$ (1 molal) to occur, but only that the potentials or driving forces of chemical reactions corresponding to the other electrodes are greater or less than this potential by the values given.

Electrode Potential and Concentration.—We have considered an electrode reaction in terms of positive electricity passing from electrode to solution, whether the actual tendency was in this direction or not, and we shall denote electrodes in which there is the opposite tendency (that of positive electricity passing from solution to electrode) by a negative electrode potential. The chlorine electrode is an example of an electrode at which the natural tendency is for positive electricity to pass from solution to electrode, but we write

$$Cl^- + \oplus = \tfrac{1}{2} Cl_2; \; E = \text{a minus quantity.}$$

In computing the effect of concentration upon electrode potential, the electrochemical reaction occurring at an electrode is always written with the symbol $\oplus$ on the left hand side[1] of the equation, and the actual sign of the electromotive force is then automatically cared for by the method of computing electrode potentials. In any cell the total potential is $E = E_1 - E_2$, where E_1 is the left hand electrode or anode potential, and E_2 is the right hand electrode potential (cathode). In computing the electromotive force of any cell, separate values of E_1 and E_2 are computed from the normal electrode potentials by the equation given below, and the total electromotive force of the cell is obtained by subtraction.

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[1] Lewis, *J. Am. Chem. Soc.*, **35,** 22 (1913).

Let the general chemical reaction for any electrode be denoted by the production of c mols of the substance C and d mols of the substance D from a mols of substance A and b mols of B by the use of n faradays of positive electricity. The chemical equation for this change is written

$$a\mathrm{A} + b\mathrm{B} + \ldots + n \oplus = c\mathrm{C} + d\mathrm{D} + \ldots$$

Further, let E^0 be the electrode potential corresponding to unit (1 molal) concentration (or pressure) of each substance involved. If the solutes produced or destroyed are gases, it is customary to insert their partial pressures in atmospheres in place of their molal concentrations, and to determine E^0 with a partial pressure of each gaseous substance of one atmosphere. Then E, the electrode potential corresponding to any other concentration of the reacting substances and reaction products, is

$$E = E^0 - \frac{RT}{nF} \ln \frac{(\mathrm{C})^c(\mathrm{D})^d}{(\mathrm{A})^a(\mathrm{B})^b}. \qquad (1)$$

In using this equation, the electrode reaction should first be written down with the $\oplus$ symbol on the left-hand side of the equation, and the proper number of faradays used to produce the reaction as written. In the logarithm term, the products of the electrochemical reaction are written in the numerator, and the substances used during the reaction are written in the denominator, just as in formulating chemical equilibrium expressions. The concentrations of reaction products, denoted by (C) and (D), are molal concentrations, not equivalent concentrations. A few examples of the use of this equation will make its meaning clearer.

For the hydrogen electrode, the potential of H_2 (1 atm.),

H^+ (1 molal) is E^0, and the electrode potential for any other concentration or pressure, corresponding to the reaction

$$H_2\ (p\ \text{atm.}) + 2\ \oplus\ = 2H^+,$$

is

$$E = E^0 - \frac{RT}{2F} \ln \frac{(H^+)^2}{p_{H_2}} \tag{2}$$

When E is expressed in volts and the faraday, denoted by F, in ampere-seconds or coulombs, the resulting energy output of the cell is in volt-ampere-seconds or joules, and R, the gas constant, should be so expressed; the numerical value being 8.316 joules. At a chlorine electrode the reaction is

$$2Cl^-\ (\text{at } C \text{ molal}) + 2\ \oplus\ = Cl_2\ (p\ \text{atm.})$$

and the electrode potential in terms of the normal chlorine electrode is

$$E = E^0 - \frac{RT}{2F} \ln \frac{p_{Cl_2}}{(Cl^-)^2} \tag{3}$$

Similarly at an electrode of iron dipping into ferrous sulfate, the electrode reaction is

$$Fe + 2\ \oplus\ = Fe^{++}$$

and the electrode potential in terms of a specific electrode potential corresponding to iron against molal ferrous ion is

$$E = E^0 - \frac{RT}{2F} \ln (Fe^{++}).$$

There is another kind of electrode reaction which causes no change in the number of mols of solute present, but only a change in the state of oxidation of the solutes. The ferrous-ferric electrode is an example; it consists of a platinum plate dipping into a solution containing ferrous ions and ferric ions. Its electrode reaction is

$$Fe^{++} + \oplus\ = Fe^{+++},$$

and the electrode potential corresponding to any concentrations of each ionic species, in terms of the potential when ferrous ions are one molal and ferric ions are one molal, is

$$E = E^0 - \frac{RT}{F} \ln \frac{(Fe^{+++})}{(Fe^{++})}.$$

Another electrode which functions as a chloride-ion electrode consists of silver coated with silver chloride and dipping into a chloride solution. The electrochemical reaction is

$$\mathrm{Ag\ (solid)} + \mathrm{Cl^-} + \oplus = \mathrm{AgCl\ (solid)},$$

and its electrode potential in a chloride ion solution of any concentration is

$$E = E^0 - \frac{RT}{F} \ln \frac{1}{(\mathrm{Cl}^-)}.$$

It should be noted that the concentrations of solid substances are not included in the logarithm term. It is not necessary to know the concentration of metallic silver or of silver chloride. Only those substances which are gases or solutes appear in the expression.

Normal Chlorine Electrode Potential.—Consider again the cell

$$\mathrm{H_2}\ (1\ \text{atm.}),\ \mathrm{HCl}\ (0.1\ m.),\ \mathrm{Cl_2}\ (1\ \text{atm.});\ E = 1.4881\ v.$$

The total electromotive force of this cell is the difference between two electrode potentials; the normal hydrogen electrode has been defined as of zero potential. Then a value of E_1 for hydrogen gas against a solution which is not one molal in hydrogen ions may be calculated in the way explained above. A similar calculation in terms of the normal chlorine electrode potential may be made for E_2. On the other hand, if the fractional ionization of hydrochloric acid is known, it is possible to calculate from the measured electromotive force of the cell involving 0.1 molal hydrochloric acid a value for the normal electrode potential of chlorine. This may be seen from the equation

$$E_1 - E_2 = 1.4881 = \left[E^0_{\mathrm{H}} - \frac{RT}{2F} \ln (\mathrm{H}^+)^2\right] - \left[E^0_{\mathrm{Cl}} - \frac{RT}{2F} \ln \frac{1}{(\mathrm{Cl}^-)^2}\right]$$

In order to be consistent in electromotive force calculations, we should employ fractional ionization values based upon potential measurements. As mentioned at the end of the chapter on Electrolytic Conduction, these are not in agreement with ionization values obtained from freezing points or conductivity ratios. The fractional ionization of 0.1 formal hydrochloric acid is 0.82 as determined from electromotive forces, in a way to be explained presently.[1] We shall use this value in computing the normal electrode potential of chlorine. Upon solving the above expression for E^0_{Cl} and noting that the hydrogen ion concentration is equal to the chloride ion concentration, we have

$$\begin{aligned} E^0_{Cl} &= -1.4881 - \left[\frac{8.316 \times 298 \times 2.303}{2 \times 96{,}500} \log\ (0.082)^4\right] \\ &= -1.360 \text{ volts at } 25^\circ. \end{aligned}$$

This is the potential of chlorine gas at one atmosphere in contact with a metal plate dipping into a solution one molal in chloride ion. Such a potential would not be observed in experiments unless the solutes were all ideal ones conforming to the simple laws of ideal solutions. But this normal electrode potential may be used to calculate the electrode potential of chlorine in chloride ion solutions which are dilute without significant error, for it has been calculated from measurements upon a dilute solution of hydrochloric acid. This potential corresponds to that of the ideal cell

$$H_2 \text{ (1 atm.)}, H^+ + Cl^- \text{ (1 molal)}, Cl_2 \text{ (1 atm.)};$$

of which the electromotive force is +1.360 volts. This change of sign is made because in calculating the total electromotive force of the cell, the expression is $E = E_1 - E_2$, and E_1 is zero by definition, whence $E = -E_2 = -E^0_{Cl}$.

In order to set up a cell of hydrogen against one molal hydrogen ion it is clearly necessary to adopt some assumption as to the fractional ionization of a strong acid at high concentration. It is customary in laboratory work to *assume* that a solution 2 normal in sulfuric acid is one molal in hydrogen ion, though it is by no means certain that the assumption is correct. The molal hydrogen electrode has been defined in an indefinite way, which is exactly what should not be done for a reference standard. A much more definite, and therefore much better, standard is the normal calomel electrode,

$$Hg + Hg_2Cl_2, \text{ KCl (1 normal)},$$

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[1] Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 2,543 (1917); Lewis, *J. Am. Chem. Soc.*, **34**, 1,643 (1912), gives 0.76; if 0.76 is used in the calculation above, −1.356 is obtained for the chlorine electrode in place of −1.360.

which is defined in terms of the total electrolyte, and is therefore a perfectly definite standard, reproducible in any laboratory without any assumption regarding ionization. Many of the electrode potentials in the following table have been computed from measurements against the normal calomel electrode by adding to these measured potentials that of the cell[1]

$$H_2 \text{ (1 atm.)}, H^+ \text{ (1 molal)} || KCl \text{ (1 molal)}, Hg_2Cl_2 + Hg,$$

for which the electromotive force has been calculated as 0.2828 volts, by several investigators.[2] In the equations above given for calculating the electromotive force of simple cells, it does not matter whether electrode potentials referred to the one or other standard electrode are used, so long as both E^0 values employed in any calculation are referred to the same standard.

When the elements are arranged in the order of decreasing electrode potential, the order is the "electromotive series" mentioned in inorganic chemistry. In electrolysis, that ion which requires the lowest discharge potential will be deposited first. For example, in electrolysis of a solution of sodium chloride, using a cathode coated with silver chloride, the reaction

$$AgCl \text{ (solid)} = Ag \text{ (solid)} + Cl^- + \oplus$$

requires a potential of − 0.2238 volts; that is, a potential which will cause this electrode reaction is still 0.2238 volts too low for the deposition of hydrogen. The potential required to deposit any ion at a cathode must be greater than its own

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[1] There is a small potential resulting from the junction of two solutions of different solutes, or a junction of two concentrations of the same solute. This small potential has been subtracted from the total cell, a fact which is indicated in cells by inserting two vertical lines between the solutions as is done above. Correcting for junction potentials is a difficult task; the potentials involved are usually only a few thousandths of a volt, and junction potentials calculated by two different investigators do not quite agree. The calculation is described by Lewis and Sargent, *J. Am. Chem. Soc.*, **31**, 363 (1909), for a junction between unlike solutes at the same concentration, and by MacInnes, *J. Am. Chem. Soc.*, **37**, 2,301 (1915), for a single solute at different concentrations on the two sides of a liquid junction.

[2] Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.*, **39**, 2,245 (1917); MacInnes, *J. Am. Chem. Soc.*, **41**, 1,086 (1919); Beattie, *J. Am. Chem. Soc.*, **42**, 1,128 (1920), finds 0.2826; Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 2,543 (1917), find 0.2824.

TABLE 119.—NORMAL ELECTRODE POTENTIALS AT 25°

Electrode	Normal hydrogen electrode as zero	Normal calomel electrode as zero	Electrode	Normal hydrogen electrode as zero	Normal calomel electrode as zero
[1] **Li**, Li^+ (1 molal)	3.0216	3.3044	**Cu**, Cu^{++} (1 molal)	−0.340	−0.060
[2] **Na**, Na^+ (1 molal)	2.7153	2.9981	**Cu**, Cu^+ (1 molal)	−0.510	−0.230
[3] **K**, K^+ (1 molal)	2.9256	3.2084	[6] **Ag**, Ag^+ (1 molal)	−0.799	−0.516
[4] **Rb**, Rb^+ (1 molal)	2.9220	3.2050	[6] **M**, $Fe^{+++} + Fe^{++}$ (1 molal)	−0.7390	−0.4560
[5] **Pb**, Pb^{++} (1 molal)	0.1295	0.4125	[10] Br_2, Br^- (1 molal)	−1.0872	−0.8039
Zn, Zn^{++} (1 molal)	0.76	1.04	[11] Cl_2 (1 atm.), Cl^- (1 molal)	−1.3623	−1.0795
Fe, Fe^{++} (1 molal)	0.43	0.71	I_2, I^- (1 molal)	−0.533	−0.250
[7] **Ag** + **AgCl**, Cl^- (1 molal)	−0.2238	−0.0590	[12] **Hg** + Hg_2Cl_2, KCl (1 molal)	−0.2828	0.0000
[7] **Hg** + Hg_2Cl_2, Cl^- (1 molal)	−0.2700	0.0128	[13] **Cu** + **CuCl**, Cl^- (1 molal)	−0.1200	0.1628
[5] **Sn**, Sn^{++} (1 molal)	+0.1435	0.4263	O_2 (1 atm.), OH^- (1 molal)	−0.393	−0.110
[12] H_2 (1 atm.), H^+ (1 molal)	0.0000	0.2828			

electrode potential or it would pass back into solution when present, therefore would not deposit from a solution at all. But the tendency of sodium ions to deposit is small, for the electrode potential of sodium is very high. The potential which will cause hydrogen to deposit is 2.715 volts below that required to deposit sodium. During this electrolysis, silver chloride will be reduced to silver until all of it is exhausted, then hydrogen ions will discharge and leave hydroxyl ions behind, forming sodium hydroxide, but sodium will not deposit at all under the conditions of electrolysis.

It will be clear from this statement that the electrode potential of sodium has not been determined by a single step. It was in fact determined in two steps, the first of which measured the potential of sodium against a dilute sodium amalgam through a solution in a non-aqueous solvent; the second step determined was the potential of this amalgam against the hydrogen electrode through sodium hydroxide solution.

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[1] Lewis and Kraus, *J. Am. Chem. Soc.*, **35**, 341 (1913).
[2] Lewis and Kraus, *J. Am. Chem. Soc.*, **32**, 1,459 (1910).
[3] Lewis and Keyes, *J. Am. Chem. Soc.*, **34**, 119 (1912).
[4] Lewis and Argo, *J. Am. Chem. Soc.*, **37**, 1,989 (1915).
[5] Getman, *J. Am. Chem. Soc.*, **40**, 619 (1918).
[6] Noyes and Brann, *J. Am. Chem. Soc.*, **34**, 1,016 (1912).
[7] Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 2,541 (1917).
[10] Lewis and Storch, *J. Am. Chem. Soc.*, **39**, 1,910 (1917).
[11] Lewis and Rupert, *J. Am. Chem. Soc.*, **33**, 299 (1911).
[12] Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.*, **39**, 2,258 (1917).
[13] Noyes and Chow, *J. Am. Chem. Soc.*, **40**, 739 (1918).

Electromotive Force and Ion Concentration.—We have already seen that a normal electrode potential can be calculated from the electromotive force of a cell involving a dilute solution. Conversely, from the measured electromotive force in a cell with some other concentration of solution, we can calculate the ion concentration. The electromotive force of the cell H_2 (1 atm.), HCl (C molal), Cl_2 (1 atm.) is $E_1 - E_2$, and each of these values may be computed from the normal or specific electrode potentials in Table 119 by means of equations (2) and (3) above, each of which equations is a special case of equation (1). But the "ion concentrations" so computed differ from the values based on fractional ionization values obtained from freezing point determinations or from the ratio of equivalent conductivities, and the differences are considerable. Thus in computing the fractional ionization of tenth normal hydrochloric acid from that of thousandth normal acid, 82 per cent is obtained by the electromotive force method, and 92 per cent from the conductivity ratio. It is the fraction 0.82 which is commonly called the "activity ratio," since in tenth normal hydrochloric acid the activity or effective concentration of hydrogen ion is 0.082. The "activity ratios" discussed briefly at the end of Chapter VI were determined in this way.

One of the serious problems in connection with the ionic theory is the lack of an adequate explanation of this difference. For very dilute solutions the activity ratios and conductivity ratios are in substantial agreement; in strong solution there is a wide difference which is not due to experimental errors. In fact, it is this serious difference which has recently led some chemists to discard the idea of fractional ionization, to assume complete ionization, and to seek some other explanation for change of activity ratio and of conductivity ratio with changing concentration. This new line of thought has not yet been sufficiently developed to warrant its consideration in detail here.[1]

Ion concentrations determined from electromotive force experiments are considered in detail later in this chapter, under the heading "concentration cells."

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[1] References to the original literature bearing on this new hypothesis will be found at the end of Chap. VI, page 183.

Electromotive Force and Chemical Equilibrium.—We shall now consider several examples of the use of normal electrode potentials in determining conditions of chemical equilibrium. It has already been stated that the driving force of a cell is the driving force of the chemical reaction taking place in it. When therefore equilibrium is reached, there is no tendency for the chemical reaction to proceed one way or the other, and there is no electromotive force. We need not set up a cell in which there is no electromotive force developed, however, in order to determine equilibrium conditions. Let us consider the cell

$$\text{Ag} + \text{AgCl, HCl (0.1 formal), Cl}_2 \text{ (1 atm)}; \ E = 1.142 \ v.$$

The hydrochloric acid in this cell is saturated with silver chloride, which gives rise to a very small concentration of silver ions such that the solubility product $(Ag^+)(Cl^-)$ is satisfied, and on account of the very small concentration involved, silver chloride is essentially completely ionized, so that this solubility product is practically S_0^2, where S_0 is its solubility in pure water. The chloride ion concentration in 0.1 formal hydrochloric acid is about 0.082; the silver ion concentration may be computed from the electromotive force. This cell may also be written

$$\text{Ag, Ag}^+ \ (c) + \text{Cl}^- \ (0.082), \text{Cl}_2; \ E = 1.142 \ v,$$

where c denotes the silver ion concentration in a solution 0.1 formal in hydrochloric acid and saturated with silver chloride. At the left hand electrode the reaction is $Ag + \oplus = Ag^+$, and

$$E_1 = E^0_{\text{Ag}} - \frac{RT}{F} \ln c.$$

At the right hand electrode the chemical reaction is

$$2\ \text{Cl}^- + 2\ \oplus = \text{Cl}_2 \text{ (1 atm.)},$$

and the electrode potential is

$$E_2 = E^0_{\text{Cl}} - \frac{RT}{2F} \ln \frac{1}{(\text{Cl}^-)^2}.$$

The difference $E_1 - E_2$ is the electromotive force of the cell. Substituting the above expressions, we have

$$1.142 = E^0_{\text{Ag}} - \frac{RT}{F} \ln c - \left[E^0_{\text{Cl}} + \frac{RT}{2F} \ln (\text{Cl}^-)^2\right]$$

$1.142 = -0.799 - 0.0592 \log c - (-1.362) - 0.0592 (-1.076)$ or, upon solving for log c,
$\log c = -8.70$; whence $c = 0.2 \times 10^{-8} = (Ag^+)$ in 0.1 formal HCl. The chloride concentration in 0.1 formal hydrochloric acid is 0.082, and the solubility product for silver chloride is $0.082 \times 0.2 \times 10^{-8} = 1.64 \times 10^{-10}$; the square root of this figure is 1.3×10^{-5}, which is the value for the solubility of silver chloride in pure water based on this calculation. Other experiments yield solubilities of 1.1 to 1.2×10^{-5}.

As another example of the application of electromotive force to chemical equilibrium, consider the reaction

$$Sn \text{ (solid)} + Pb(ClO_4)_2 = Pb \text{ (solid)} + Sn(ClO_4)_2$$

for which equilibrium data has been given in a previous chapter, showing the ratio $(Sn^{++})/(Pb^{++}) = 2.98$ from a purely chemical method of experiment. At equilibrium the electromotive force of the cell

$$Sn,\ Sn(ClO_4)_2 + Pb(ClO_4)_2,\ Pb$$

will be zero, whence E_1 is equal to E_2. We shall compute the two electrode potentials, equate them, and solve for the ratio $(Sn^{++})/(Pb^{++})$, following the method already used on other electrodes. The electrode potential of the tin electrode is

$$E_1 = E^0_{Sn} - \frac{RT}{2F} \ln (Sn^{++}),$$

corresponding to the chemical equation $Sn + 2 \oplus = Sn^{++}$; and at the lead electrode the chemical reaction written in the usual way is $Pb + 2 \oplus = Pb^{++}$, for which the electrode potential is

$$E_2 = E^0_{Pb} - \frac{RT}{2F} \ln (Pb^{++}).$$

Equating these two electrode potentials and solving for the ratio of tin to lead in solution, we have

$$E^0_{Sn} - E^0_{Pb} = \frac{RT}{2F} \ln \frac{(Sn^{++})}{(Pb^{++})}$$

whence

$$\log \frac{(Sn^{++})}{(Pb^{++})} = \frac{0.1435 - 0.1249}{0.0296} = 0.473; \text{ and } \frac{(Sn^{++})}{(Pb^{++})} = 2.97.$$

This illustrates a method of obtaining equilibrium data from specific electrode potentials, or a method of calculating one electrode potential from another by means of equilibrium measurements.[1]

Ionization Constant of Water.—From measurements of cells of the type,

$$H_2, KOH, KCl, HCl, H_2$$

there is obtained, after correction for the liquid potentials between the alkali and salt solution, and between the salt solution and acid, an electromotive force which is equivalent to that of a cell[2]

$$H_2 \text{ (1 atm.)}, OH^- || H^+, H_2 \text{ (1 atm.)};$$

and with molal hydrogen ion on the right hand side and molal hydroxide ion on the left hand side, the measured electromotive force at 25° is 0.8278 volts. The ionization constant of water is the product of the ion concentrations of hydrogen and hydroxide ions in any solution. In the left hand solution hydrogen ions exist in exceedingly small concentration, but this concentration may be calculated from the electrode potential, since this cell may be considered as equivalent to

$$H_2 \text{ (1 atm.)}, H^+ \text{ (at } C) || H^+ \text{ (1 molal)}, H_2 \text{ (1 atm.)}$$

for which E_2 is zero, and hence E_1 is the measured electromotive force of the cell. Then

$$E_1 = 0.8278 = E^0_{\mathrm{H}} - \frac{RT}{F} \ln C = 0 - 0.0592 \log C$$

$$\log C = -\frac{0.8278}{0.0592} = -14.0.$$

Then the concentration of hydrogen ion in the presence of molal hydroxide ion is 10^{-14}, and this is the value of $K_w = (H^+)(OH^-)$ sought.[3]

Titration in Colored or Turbid Solutions.—It is sometimes desired to titrate to neutrality a solution which is so cloudy that ordinary color indicators are useless. This may be accomplished readily by means of electromotive force measurements, since near the end point of a titration the hydrogen ion concentration changes rapidly. Suppose a platinum plate to dip into the solution to be titrated, hydrogen to bubble over the plate, and connection to be established with a normal calomel electrode through a very small tube so that none of the unknown solution is lost. Table 120 below shows the concentration of hydrogen ion at several stages of a titration, supposing 100 c.c. of 0.20 normal acid to be titrated with 0.20 normal alkali. For example, when 99 c.c. of alkali have been added, assuming a strong acid to be present, only 1 per cent of the acid remains untitrated, the total volume of solution has increased to 199 c.c., and it contains 0.0002 formula weights of acid, hence the acid concentration is now approximately 0.001 normal. When 99.9 c.c. of alkali have been added, the acid concentration is 0.0001 normal; when 100 c.c. have been added, the hydrogen ion concentration is that of pure water, and for 100.1 c.c. of alkali the solution is made 0.0001 normal in hydroxide ions, or $10^{-14}/0.0001 = 10^{-10}$ in hydrogen ions. Thus the last 2 drops change the logarithm of the hydrogen ion concentration from -4 to -7, and the first drops in excess change it from -7 to -10. Each of these changes corresponds to a

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[1] Noyes and Toabe, *J. Am. Chem. Soc.*, **39**, 1,537 (1917).

[2] Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.*, **39**, 2,245 (1917).

[3] Similar results are obtained by Lorenz and Bohi, *Z. physik. Chem.*, **66**, 733 (1909), from a cell H_2, HCl (0.1 *f.*) || KOH (0.1 *f.*), H_2; $E = 0.6980$ at 25°. Assuming each solution to be 82 per cent dissociated, log K_w is -13.9 and K_w is 1.2×10^{-14}.

TABLE 120.—HYDROGEN ION CONCENTRATION IN A SOLUTION OF ACID DURING TITRATION WITH ALKALI

Volume of 0.2 normal base added to 100 c.c. of 0.2 normal acid	Hydrogen ion concentration if the acid is		Electromotive force for	
	Hydrochloric acid	Acetic acid	Hydrochloric acid	Acetic acid
98.0	1.9×10^{-3}	2×10^{-7}	0.443	0.679
99.0	9.5×10^{-4}	10^{-7}	0.462	0.707
99.5	4.7×10^{-4}	5×10^{-8}	0.477	0.715
99.8	2×10^{-5}	2×10^{-8}	0.561	0.739
100.0	10^{-7}	10^{-9}	0.697	0.816
100.2	5×10^{-11}	5×10^{-11}	0.893	0.893
100.5	2×10^{-11}	2×10^{-11}	0.917	0.917
101.0	10^{-11}	10^{-11}	0.934	0.934
102.0	5×10^{-12}	5×10^{-12}	0.952	0.952

change of nearly 0.18 volt in the electromotive force of the cell of which the unknown solution forms a part. Therefore a plot of observed electromotive force against the number of cubic centimeters of alkali added would show a sharp rise at the end point.

This is illustrated in Fig. 61 below, for a strong acid, and for acetic acid, whose salt is hydrolyzed in dilute solution. It will be noted that in both cases there is a sharp break in the curve of measured electromotive force plotted against volume of base added, which indicates clearly the endpoint of the titration. Such a process is especially useful in connection with biological experiments. Similar curves showing complete oxidation of a ferrous salt to ferric salt may be obtained by plotting the buret readings against measured potential. Such electrometric titrations are beginning to receive the attention they deserve from analytical chemists. As the change in potential at the endpoint is relatively large, no sensitive galvanometer is required, and

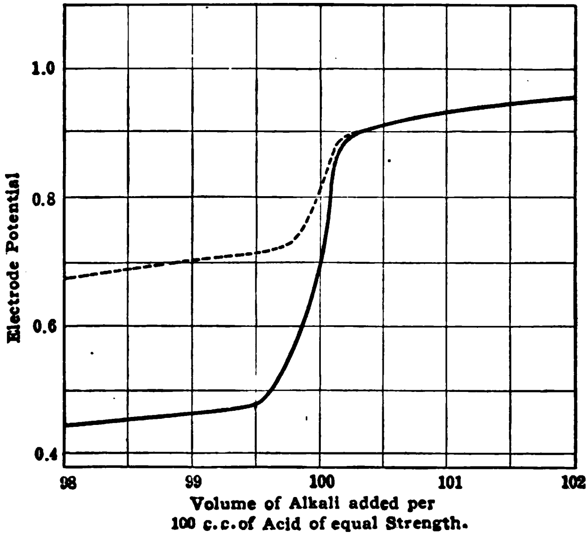

FIG. 61.—Showing change of electromotive force with progress of titration. The cell consists of a hydrogen electrode dipping into an acid solution, and connected to a normal calomel electrode. (Hydrochloric acid is shown by a solid line, acetic acid by the dotted line.)

relatively simple apparatus for such experiments may now be had in the market.

Concentration Cells.—When two separate cells which differ only in the concentration of electrolyte in them are connected in opposition, and positive electricity is passed through the whole combination, the net effect is the transfer of solute from one concentration to another. As an example, consider the cells

$$AgCl + Ag,\ HCl\ (C_1),\ H_2 \frown H_2,\ HCl\ (C_2),\ AgCl + Ag.$$

When a faraday of electricity is passed through the whole system considered as a single cell, the electrode reactions are $Ag + \oplus + Cl^- = AgCl$ and $H^+ = \frac{1}{2}H_2 + \oplus$ in the first cell, and $\frac{1}{2}H_2 + \oplus = H^+$ and $AgCl = Ag + \oplus + Cl^-$ in the second cell. The net effect of these two cells is therefore the formation of a mol of hydrogen chloride in the second cell and the loss of it in the first cell. For dilute acid solutions the electromotive force of the whole combination, considered as a single concentration-cell is shown by the equation

$$E = \frac{nRT}{F} \ln \frac{C_1\gamma_1}{C_2\gamma_2} \tag{4}$$

where n is the number of mols of ion solute transferred from the ion concentration $C_1\gamma_1$ to the concentration $C_2\gamma_2$ per faraday of electricity. In this expression a mol of hydrogen ion is considered a mol of solute and a mol of chloride ion as another mol of solute and hence $n = 2$ for hydrochloric acid. The expression is not accurate for solutions above 0.01 normal; in order to make it strictly accurate, in place of the ion concentration as computed from concentration and conductivity ratio, $C_1\gamma_1$, this ion concentration must be determined independently from other electromotive force measurements. In other words, the "activity" or proper mass-action effect should be used in place of the ion concentration computed from total concentration and fractional ionization.

Such calculations of ion activity in one solution from that in another solution of the same solute at a different concentration may be based on electromotive force measurements of single cells of the type

$$H_2\ (1\ \text{atm.}),\ HCl\ (C),\ AgCl\ (\text{solid}) + Ag.$$

Measurements for this cell at several temperatures[1] and for various concentrations of hydrochloric acid are given in Table 121.

TABLE 121.—ELECTROMOTIVE FORCE OF THE CELL H_2, HCl, AgCl + Ag

Mols HCl per 1,000 grams water	Electromotive force at		
	15°	25°	35°
0.33314	0.29678	0.29348	0.28958
0.10000	0.35375	0.35221	0.35031
0.09534	0.35600	0.35453	0.35270
0.03324	0.40530	0.40545	0.40513
0.00948	0.46452	0.46666	0.46824
0.003378	0.51325	0.51696	0.52023

If the first two of these cells are connected in opposition at 25°, the net electromotive force is the difference between those of the separate cells, and the change in state of the system as a whole is a transfer of hydrochloric acid from one solution to the other. If the transfer takes place from the stronger into the more dilute solution, the electromotive force is 0.05873 volt. Assuming the activity coefficient in 0.1 formal hydrochloric acid to be 0.82 (from Table 75), the activity of each ion in the stronger solution may be computed from equation (4). Two mols of solute are transferred per faraday of electricity, a mol of hydrogen ion and a mol of chloride ion. Then

$$0.0587 = \frac{2 \times 8.316 \times 298 \times 2.303}{96{,}500} \log \frac{a_2}{0.082};$$

whence $\log \frac{a_2}{0.082}$ is 0.496, and a_2 is 0.257 in a solution in which the acid concentration is 0.333. The activity coefficient, or "corrected" degree of ionization, is therefore 0.257/ 0.333 = 0.78.

In place of taking 0.82 as the activity coefficient in 0.1 formal hydrochloric acid, we might assume that the activity coefficient and the fractional ionization as determined by conductivity ratio were in agreement in a solution as dilute as 0.00338 formal.

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[1] Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 3,532 (1917.)

Assuming this, the activity coefficient in solutions of other concentrations may be calculated from equation (4) by taking the difference between the electromotive force of the most dilute cell and that involving any other concentration of acid. When this is done, activity coefficients in substantial agreement with those of Table 75 on page 183 are obtained. From this particular set of data the values are:

Acid concentration	0.333	0.1000	0.03324	0.00948	0.003378
Activity coefficient	0.782	0.821	0.876	0.934	0.985

The failure of equation (4) to agree with measured electromotive forces for concentration cells involving strong solutions is one of the serious faults of our present theory of solutions. The equation, like all other equations for solutions which contain the gas constant R, assumes an ideal solute, one whose osmotic pressure is equal to the pressure of solute alone if confined in a space equal to that occupied by the solution. But as stated before, the "fractional ionization" which may be derived for one solution from measured electromotive forces, if that of the other is known, is not in agreement with fractional ionization computed from freezing point depression or from the conductivity ratio.

Amalgam Concentration Cells.—Deviations of equation (4) from experiment are not confined to aqueous solutions of ionized salts; a similar effect is observed in concentration cells consisting of amalgams of thallium (and other metals) in mercury. For example, a cell at 15° composed of two amalgams containing different amounts of thallium and in contact with a solution of thallous chloride,

$$\mathrm{Hg + Tl}\ (0.410\%),\quad \mathrm{TlCl},\quad \mathrm{Hg + Tl}\ (0.111\%),$$

operates by transferring thallium from one amalgam to the other. At the left hand side the reaction is $\mathrm{Tl} + \oplus = \mathrm{Tl}^+$, and at the right it is $\mathrm{Tl}^+ = \mathrm{Tl} + \oplus$. Applying the above equation to calculate the electromotive force of this cell, we find

$$E = \frac{8.32 \times 288 \times 2.303}{96{,}500} \log \frac{0.410}{0.111} = 0.0340,$$

while actual experiment[1] gives 0.0348; the difference is 2.5

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[1] Richards and Wilson, *Carnegie Inst. Publ.*, 118, 22 (1909).

per cent of the measured value. Similar experiments with indium amalgams lead to somewhat better agreement between observed and calculated potentials, but the potential between tin amalgams containing respectively 0.66 per cent and 0.20 per cent of tin by weight is only 85 per cent of that calculated from the ideal equation above. In all of the amalgam cells, results approaching those derived from the concentration equation were obtained as the amalgams employed were made more and more dilute.[1]

There is another type of concentration cell whose change in state corresponds only to the transfer of a solute from one concentration to another, but which involves only a single set of electrodes. As an example we may consider the cell

$$H_2,\ HCl\ (C_2),\ HCl\ (C_1),\ H_2,$$

and pass one faraday of positive electricity through it. The electrode reactions are $\frac{1}{2}H_2 + \oplus = H^+$ at the left and $H^+ = \frac{1}{2}H_2 + \oplus$ at the right, hence by electrolysis there has been formed at the left one mol of hydrogen ion into a concentration C_2, and there has been removed from solution at C_1 one equivalent of hydrogen ion. Electricity is carried *through* the solutions by hydrogen ions and chloride ions in quantity proportional to their respective ionic velocities. That is, denoting by T_{Cl} the transference number of chloride ions, for each faraday of electricity carried through the cell T_{Cl} faradays will be carried by T_{Cl} equivalents of chloride ion moving from right to left, and $(1 - T_{Cl})$ faradays will be carried by hydrogen ions moving from left to right. Then the left hand portion of the cell will gain by transference T_{Cl} equivalents of chloride ion and lose by transference $(1 - T_{Cl})$ equivalents of hydrogen ion. Its net effect per faraday is the gain of T_{Cl} equivalents of both hydrogen ion and chloride ion. At the right hand electrode T_{Cl} equivalents of chloride ions are lost by transference, and $(1 - T_{Cl})$ equivalents of hydrogen ion are gained by transference. Hence the net effect is the loss of T_{Cl} equivalents of hydrogen ion and of chloride ion when the effects of both electrolysis and transference are considered. Considering now the cell as a whole, each faraday of electricity results in transferring T_{Cl} equivalents of hydrochloric acid from the right hand side of the cell to the left hand side. Applying the formula given above for concentration cells, and considering hydrogen ion and chloride ion as each constituting a mol of solute, we have $n = 2T_{Cl}$, and

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[1] See also Richards and Daniels, *J. Am. Chem. Soc.*, **41**, 1,732 (1919).

$$E = \frac{2T_{Cl}RT}{F} \ln \frac{C_1\gamma_1}{C_2\gamma_2}. \tag{5}$$

From electromotive force measurements of cells of this type (called cells with transference) and of the type first given (called cells without transference) it is possible to determine the transference number, since it will be seen upon dividing equation (4) by equation (5) that the ratio of the electromotive forces is the transference number direct.[1]

Electromotive Force and Heat of Reaction.—Chemical reactions which proceed vigorously evolve large quantities of heat in many cases. When these same reactions are caused to take place in electric cells or batteries, electrical energy is given out in place of heat. Naturally a given quantity of energy cannot appear as heat and still be used to generate electricity. In many cells the quantity of electric energy is roughly equal to the heat of the reaction when carried out in a calorimeter, and it was at first thought that the electromotive force of a cell could be computed from the heat effect simply by equating EnF to Q, the heat of reaction. In order to test this belief, it is only necessary to place an electric cell in a calorimeter and let it operate. If any heat is given to the calorimeter during the electric operation of the cell, the simple equivalence of total heat of reaction and EnF is not to be expected, for some heat is evolved even by the electric process. If during its operation the cell absorbs heat from the calorimeter, the electric energy output will be greater than the heat of reaction by the quantity of heat absorbed from the calorimeter and changed into electric energy. Usually there is not a very large evolution or absorption of heat during the operation of an electric battery, and the relation given above, $EnF = Q$, is *roughly* satisfied in many batteries.

---

[1] Examples of such measurements are given by MacInnes and Parkers *J. Am. Chem. Soc.*, **37**, 1,445 (1915), for potassium chloride, and by MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1,117 (1920), for lithium chloride. These papers will be difficult reading for beginners, but are very profitable reading for anyone really interested in the method.

A strict relation between electromotive force and heat of reaction is that known as the Gibbs-Helmholtz equation,

$$\frac{EnF - Q}{T} = nF\frac{dE}{dT} \tag{6}$$

where dE/dT is the rate of increase of electromotive force with increasing temperature. It will be seen from the equation that when dE/dT is zero, that is, when the electromotive force does not change with temperature, the heat of reaction Q is equal to the electric energy EnF derived from the cell. In other words, the approximation that the heat of a reaction is equal to the electric energy derivable from it is more nearly true the smaller the temperature coefficient of electromotive force. In using the Gibbs-Helmholtz equation the heat of reaction Q must be expressed in joules since the term EnF appearing beside it is in joules. A calorie is 4.182 joules.

The integral of this equation between two temperature limits over which the heat of reaction is substantially constant is

$$\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{Q}{nF}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{7}$$

Let us illustrate the application of this equation by means of the second cell of Table 121, using E_2 as the electromotive force at 35°, where T is 308°. The chemical reaction corresponding to two faradays passing through the cell is

H_2 (1 atm.) + 2AgCl (solid) = 2HCl (in 0.1 *f.*) + 2Ag (solid) + Q, and upon substituting in equation (7), it is a value for this heat of reaction which is obtained:

$$\frac{0.35031}{308} - \frac{0.35375}{288} = \frac{Q}{2 \times 96{,}500}\left(\frac{1}{308} - \frac{1}{288}\right).$$

whence Q is 77,870 joules or 18,900 cal.

The heat of dilution of hydrochloric acid may also be calculated from Table 121 by means of equation (7). Since when two cells are connected in opposition, the net effect of the pair is the transfer of hydrogen chloride from one concentration to another, the electromotive force at 15° of such a pair is 0.05922 if the first two cells of Table 121 are used to transfer hydrochloric acid from 0.33314 formal to 0.1000 formal; the corresponding electromotive force at 35° is 0.06312 volts. Substitution in equation (7) leads to a value of the heat of dilution as follows:

$$2\mathrm{HCl}\ (\text{at } 0.333\, f.) = 2\mathrm{HCl}\ (\text{at } 0.10\, f.) + (Q = 520 \text{ joules}).$$

Questions

1. The electromotive force of a certain cell is higher at 25° than at 0°C. Does it evolve heat during its electric operation or absorb heat?

2. Calculate from the normal electrode potentials the electromotive force of the cell Hg + $HgCl_2$, HCl (0.1*m*.), Cl_2 (1 atm.). The experimentally determined value is 1.0896 volts.

3. When one mol of hydrogen chloride is formed from its elements, 22,000 cal. are evolved, and when this is dissolved in 10 liters of water, 17,200 cal. are evolved. From these data and the electromotive force of the cell H_2, HCl (0.1 *f*.), Cl_2 ($E = 1.4881$), at 25° calculate the electromotive force of this cell at 0°C.

4. Calculate the electromotive force of the cell H_2, (1 atm.), HCl (0.001 *f*.), Cl_2 (1 atm.) at 25°, assuming 98 per cent ionization.

5. Calculate the "activity" or effective concentration of hydrogen ions and of choride ions in 0.10 formal HCl from the measured electromotive force given in the text, and the normal electrode potentials.

6. The electrode potential of zinc is 0.76 volt; that of cadmium is about 0.42 volt. Calculate the equilibrium constant for the chemical reaction $ZnSO_4 + Cd = CdSO_4 + Zn$ at 25°.

7. Compute the electromotive force of the combination at 25°:

H_2, HCl (0.1*n*), $\mathrm{HgCl} + \mathrm{Hg} \frown \mathrm{Hg} + \mathrm{HgCl}$, HCl (0.001*n*), H_2. Use the data of Table 67 for the conductivity of hydrochloric acid. (Tolman and Ferguson, *J. Am Chem. Soc.*, **34**, 232 (1912).)

8. Calculate the electromotive force of the cell Zn, $ZnSO_4$ (C_1), $ZnSO_4$ (C_2), Zn, at 25° when the first solution is 0.10 formal in zinc ion and the second is 0.0001 formal in zinc ion.

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